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## (54) INK JET RECORDING METHOD

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide an ink jet recording method in which even if a recording sheet, on which records are made by using an aqueous recording liquid, is preserved under conditions of high temperatures and humidities, cracks are not generated.

**SOLUTION:** In a recording method in which a record is set on a recording paper, in which polyvinyl alcohol, inorganic fine particles, and boric acid or salt thereof are contained in an ink absorption layer on a non-water-absorption supporting body, using an aqueous recording liquid containing compounds having hydroxyl groups, as high boiling point organic solvent, a maximum amount of hydroxyl group in a high boiling point organic solvent contained in the printed recording paper, per unit area thereof, is specified so as to satisfy a condition of  $0.05 \leq X/Y \leq 0.5$  and a condition of  $Z/Y \leq 4$  as well. In the equations, X shows amounts (millimole/m<sup>2</sup>) of boric acid or its salt contained in an ink absorption layer of the recording paper, Y shows amounts (millimole/m<sup>2</sup>) of hydroxyl group in polyvinyl alcohol contained in an ink absorption layer of the recording paper, and Z shows the maximum amount (millimole/m<sup>2</sup>) of hydroxyl group in a high boiling point organic solvent contained per unit area of printed recording paper when records are set on the recording paper using aqueous recording liquid at a maximum delivery rate.

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**CLAIMS**

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[Claim(s)]

[Claim 1] In the ink jet record form which contains polyvinyl alcohol, a non-subtlety particle and a way acid, or its salt in the ink absorption layer on a non-absorptivity base material In the ink jet record approach which records the compound which has a hydroxyl group using an ink jet recording device with the aquosity recording ink contained as a high-boiling point organic solvent The way acid of the per [ unit area ] contained in the ink absorption layer of a record form, or the amount of the salt, When the amount of the hydroxyl group per unit area in the polyvinyl alcohol contained in the ink absorption layer of a record form and aquosity recording ink are printed by the maximum delivery in a record form, The ink jet record approach characterized by making the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form into the amount which is satisfied with coincidence of following condition \*\* and condition \*\*.

condition \*\* — the way acid of the per [ unit area ] by which X is contained in the ink absorption layer of a record form among  $0.05 \leq X/Y \leq 0.5$  condition \*\*  $Z/Y \leq 4$  type, or the amount (millimol / m<sup>2</sup>) of the salt Y is the amount (millimol / m<sup>2</sup>) of the hydroxyl group per unit area in the polyvinyl alcohol contained in the ink absorption layer of a record form.

Z is the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form when aquosity recording ink is printed by the maximum delivery in a record form (millimol / m<sup>2</sup>).

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]**

**[0001]**

**[Industrial Application]** This invention relates to the ink jet record approach performed in more detail using the ink jet record form which prevented degradation of the coat after printing, and which has the ink absorption layer of the opening mold which has high ink absorptivity about the ink jet record approach which records on an ink jet record form by using water color ink.

**[0002]**

**[Description of the Prior Art]** although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-color-izing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, amelioration progresses from both sides of ink and equipment, and it has spread quickly in various fields, such as various printers, facsimile, and a computer terminal, current.

**[0003]** The detail is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

**[0004]** As an ink jet record form, various record forms are used from the former. For example, the ink jet record form which painted the ink absorption layer as a record layer on the base material which consists of a regular paper, a hydrophilic binder and various kinds of coated paper which painted the layer which consists of an inorganic pigment (art paper, coat paper, cast coated paper, etc.), various kinds of papers that covered both sides with plastic resin, transparence, or various kinds of opaque plastic film is used further.

**[0005]** The above-mentioned ink absorption layer is roughly divided into the ink absorption layer of the opening mold which prepared the opening into the ink absorption layer of the swelling mold constituted by the subject in the hydrophilic binder, and the record layer.

**[0006]** The ink absorption layer of an opening mold holds ink to the opening formed in the layer, and the opening is formed by making various kinds of inorganic solid-state particles and organic solid-state particles contain in a coat.

**[0007]** As an ink jet record form, when a printing dot laps [ that the concentration of a printing dot is high and a color tone is brightly skillful, and absorption of ink ] early, ink flows out or it spreads, or the diffusion to the longitudinal direction of not carrying out and a printing dot is not large beyond the need, and engine performance, such as the circumference being smooth and not fading, is required.

**[0008]** when the ink rate of absorption of an ink absorption layer is slow, in case the liquid ink drop of two or more colors laps and is recorded, the color of each other in the border area of a color which the drop of ink causes a HAJIKI phenomenon on a record form, and produces nonuniformity and is different is \*\*\*\* — since it \*\* and image quality is reduced greatly, it is required that high ink absorptivity should be given to an ink jet record form.

**[0009]** In order to solve these problems For example, the record form which carried out humidity of the coating for surface treatment to the low size stencil paper indicated by JP,52-53012,A, The record form which prepared the coated layer of ink absorptivity in the support surface indicated by JP,55-5830,A, The record form which contains non-colloid silica powder as a pigment in the enveloping layer indicated by JP,56-157,A, The record form which used together the inorganic pigment indicated by JP,57-107878,A and the organic pigment, The record form which has two hole distribution peaks indicated by JP,58-110287,A, The record form which consists of a vertical two-layer porous layer indicated by JP,62-111782,A, The record form which has the indeterminate form crack indicated by JP,59-68292,A, the 59-123696 official report, the 60-18383 official report, etc., The record form which has the fines non-layer indicated by JP,61-135786,A, the 61-148092 official report, the 62-149475 official report, etc., JP,63-252779,A, JP,1-108083,A, The record form containing the pigment which has the specific physical-properties value indicated by the 2-136279 official report, the 3-65376 official report, the 3-27976 official report, etc., or a particle silica, JP,57-14091,A, a 60-219083 official report, a 60-210984 official report, A 61-20797 official report, a 61-188183 official report, JP,5-278324,A, The record form containing

particle silicas, such as a colloid silica indicated by the 6-92011 official report, the 6-183134 official report, the 7-137431 official report, the 7-276789 official report, etc., And JP,2-276671,A, a 3-67684 official report, a 3-215082 official report, Very many techniques, such as a record form containing the hydrated alumina particle indicated by the 3-251488 official report, the 4-67986 official report, the 4-263983 official report, the 5-16517 official report, etc., are proposed.

[0010] In an ink jet record form, although it is desirable if it has a high absorption capacity and ink absorptivity and carries out from a viewpoint of absorption of ink when absorptivity is in the base material itself, there is a problem of a base material lenticulating, and Siwa being generated on an image or being [ a color permeates partially into a base material and ] hard to come after ink jet record out of concentration.

[0011] Although the above-mentioned fault was not generated but the clear image with high concentration was obtained when a base material was non-absorptivity, there was a problem that the amount of the opening which absorbs the ink formed into an ink absorption layer received a limit.

[0012] For example, in the ink absorption layer whose desiccation thickness is 40 micrometers, although there will be only the amounts of openings of only 18 ml/m<sup>2</sup> per two 1m of ink jet record forms and it will be based also on a recording method if it is \*\*\*\*\* in which solid content can form a coat with a thickness of 22 micrometers, the case where the capacity of the opening which absorbs ink near the amount of the maximum ink runs short may arise.

[0013] If spreading thickness is increased, high void volume will be obtained, but if spreading thickness is increased, a coat will become brittle and the problem that a crack arises under low humidity or the adhesive property over a base material falls will arise.

[0014] These people proposed the approach of improving the film formation nature of a coat, and brittleness, by adding the hydrophilic binder which forms opening structure, and the hardening agent which can construct a bridge, in order to solve the above-mentioned trouble. (Japanese Patent Application No. No. 283636 [ eight to ]) The ink jet record form of the opening mold which used polyvinyl alcohol as a hydrophilic binder, used a way acid or its salt as a hardening agent, and formed the ink absorption layer of an opening mold is especially desirable as an ink jet record form.

[0015] However, when ink jet record was carried out to the ink jet record form which has the ink absorption layer were using polyvinyl alcohol as the above-mentioned hydrophilic binder, and using a way acid or its salt as a hardening agent by the water color ink which contains the compound which has a hydroxyl group as a high-boiling point organic solvent and the recorded form was saved under an elevated temperature and highly humid, it became clear that the problem which a crack produces in a coat arose partially.

[0016] When many things were examined about this cause, it became clear that it was for a coat to deteriorate according to an operation of the compound containing the hydroxyl group contained in aquosity recording ink.

[0017] Moreover, when the content of the non-subtlety particle used in order that this crack may form an opening is less than two in a weight ratio to polyvinyl alcohol, in order to form an opening, considering hardly generating, it is presumed that the non-subtlety particle used so much is for reducing the film formation nature of the polyvinyl alcohol in the printing section.

[0018]

[Problem(s) to be Solved by the Invention] It is made in view of the above-mentioned actual condition, and this invention is the purpose of this invention, When ink jet record is carried out to the ink jet record form which has the ink absorption layer were using polyvinyl alcohol as the above-mentioned hydrophilic binder, and using a way acid or its salt as a hardening agent with the aquosity recording ink which contains the compound which has a hydroxyl group as a high-boiling point organic solvent, even if it saves the recorded form under high-humidity/temperature, it is in offering the ink jet record approach which does not produce a crack.

[0019]

[Means for Solving the Problem] The above-mentioned technical problem in the ink absorption layer on a non-absorptivity base material Polyvinyl alcohol, In the ink jet record approach which records the compound which uses an ink jet recording device for the ink jet record form containing a non-subtlety particle and a way acid, or its salt, and has a hydroxyl group with the aquosity recording ink contained as a high-boiling point organic solvent The way acid of the per [ unit area ] contained in the ink absorption layer of a record form, or the amount of the salt, When the amount of the hydroxyl group per unit area in the polyvinyl alcohol contained in the ink absorption layer of a record form and aquosity recording ink are printed by the maximum delivery in a record form, The ink jet record approach characterized by making the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form into the amount which is satisfied with coincidence of following condition \*\* and condition \*\*.

[0020] condition \*\* — the way acid of the per [ unit area ] by which X is contained in the ink absorption layer of a record form among  $0.05 \leq X/Y \leq 0.5$  condition \*\*  $Z/Y \leq 4$  type, or the amount (millimol / m<sup>2</sup>) of the salt Y is the amount (millimol / m<sup>2</sup>) of the hydroxyl group per unit area in the polyvinyl alcohol contained in the ink absorption layer of a record form.

Z is the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form when aqueous recording ink is printed by the maximum delivery in a record form (millimol / m<sup>2</sup>).

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[0021] This invention is explained to a detail below.

[0022] The ink jet record form used for this invention has the ink absorption layer (it may be hereafter called an opening layer) of an opening mold on a non-absorptivity base material.

[0023] In this invention, since voidage high in an opening layer is obtained, polyvinyl alcohol is used as a hydrophilic binder. Since an interaction is considered as a non-subtlety particle and it is easy to form flocculation, polyvinyl alcohol can form an opening efficiently.

[0024] Cation denaturation polyvinyl alcohol, Nonion denaturation polyvinyl alcohol, and anion denaturation polyvinyl alcohol are also contained in the polyvinyl alcohol as used in the field of this invention.

[0025] Considering the viewpoint which improves film formation nature, the average degree of polymerization of polyvinyl alcohol has that desirable of 1000–5000, and 2000 especially or more are desirable.

[0026] Whenever [ saponification / of polyvinyl alcohol ] has 70 – 100% of desirable thing, and 80 – 100% of especially its thing is desirable.

[0027] Cation conversion polyvinyl alcohol is polyvinyl alcohol which has the 1–3rd class amino group which is indicated by JP,61–10483,A, and the 4th class ammonium in the main \*\* of polyvinyl alcohol, or a side chain, and it is obtained by saponifying the copolymer of the ethylenic unsaturated monomer and vinyl acetate which have a cationic radical.

[0028] As an ethylenic unsaturated monomer which has a cationic radical For example, TORIMECHIRU–(2–acrylamide –2, 2–dimethyl ethyl) ammoniumchloride, TORIMECHIRU–(3–acrylamide –3, 3–dimethyl propyl) ammoniumchloride, N–vinyl imidazole, N–vinyl–2–methylimidazole, N–(3–dimethylaminopropyl) methacrylamide, Hydroxyl ethyl trimethylammonium chloride, TORIMECHIRU–(methacrylamide propyl) ammoniumchloride, N–(1 and 1–dimethyl–3–dimethylaminopropyl) acrylamide, etc. are mentioned.

[0029] the copolymer of the ethylenic unsaturated monomer and vinyl acetate which have a cationic radical — setting — the ratio of a cation denaturation radical content monomer — vinyl acetate — receiving — 0.1–10–mol % — it is 0.2–5–mol % preferably.

[0030] The copolymer of vinyl alcohol which is indicated by the polyvinyl alcohol and JP,61–237681,A which have an anionic radical which is indicated by JP,1–206088,A as anion denaturation polyvinyl alcohol, for example, and the 63–307979 official report, and the vinyl compound which has a water-soluble radical, and the denaturation polyvinyl alcohol which has a water-soluble radical which is indicated by JP,7–285265,A are mentioned.

[0031] The polyvinyl alcohol derivative which added a polyalkylene oxide radical which is indicated by JP,7–9758,A to a part of vinyl alcohol as Nonion denaturation polyvinyl alcohol, for example, and the block copolymer of the vinyl compound and vinyl alcohol which have the hydrophobic radical indicated by JP,8–25795,A are mentioned.

[0032] Other hydrophilic binders can be made to contain with polyvinyl alcohol in an opening layer. As for other hydrophilic binders, it is desirable that it is 20 or less % of the weight in general to polyvinyl alcohol.

[0033] In this invention, the non-subtlety particle is used in order to form an opening in an ink absorption layer.

[0034] As a non-subtlety particle, white inorganic pigments, such as precipitated calcium carbonate, whiting, a magnesium carbonate, a kaolin, clay, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc hydroxide, zinc sulfide, zinc carbonate, a hydrotalcite, aluminum silicate, the diatom earth, a calcium silicate, a magnesium silicate, synthetic amorphous silica, colloidal silica, an alumina, a colloidal alumina, pseudo-boehmite, an aluminum hydroxide, a lithopone, a zeolite, and a magnesium hydroxide, etc. can be mentioned, for example.

[0035] Homogeneity may distribute in the binder with the primary particle, and a non-subtlety particle forms secondary floc and may be distributed by homogeneity in the binder.

[0036] As for a non-subtlety particle, it is desirable from an glossy viewpoint that the particle size of a primary particle uses a thing 30nm or less.

[0037] When the mean diameter of a primary particle uses the non-subtlety particle exceeding 30nm and the water-soluble polymer mordant of a cation mold is used as a mordant, floc which the water-soluble polymer mordant of a cation mold and condensation become easy to take place, and formed will also be made big and rough more, and glossiness will fall. Especially the particle size of a desirable primary particle is 20nm or less.

[0038] Especially although especially the minimum of the particle size of a primary particle is not limited, 3nm or more is 6nm or more in general from the viewpoint on manufacture of a particle.

[0039] The mean particle diameter of a non-subtlety particle observes the particle which appeared in the cross section and front face of the particle itself or an opening layer with an electron microscope, and is called for as the arithmetic average value (individual number average) in quest of the particle size of the particle of 100 arbitration. The particle size of the particle of each [ here ] is expressed with the diameter when assuming a circle equal to the projected area.

[0040] As an inorganic particle, it is desirable that it makes the ratio of the non-subtlety particle which exceeds 50nm in this case 50 or less % of the weight to all inorganic particles although the mean particle diameter of a primary particle is possible also for the non-subtlety particle and mean particle diameter of 50nm or less using together a non-subtlety particle 50nm or more, and 20 or less % of the weight is more desirable.

[0041] Considering the point of that a clear image is recordable, being able to manufacture by low cost that an image with high concentration is formed, as a non-subtlety particle, it is desirable to use the non-subtlety particle chosen from the particle silica and colloidal silica which were compounded by the gaseous-phase method, and it is most desirable to use the silica compounded by the gaseous-phase method.

[0042] The particle silica compounded by the gaseous-phase method can burn and obtain a silicon tetrachloride at an elevated temperature with hydrogen and oxygen, and is usually silica powder whose particle diameter of a primary particle is 5-500nm. What has the primary particle diameter of 30nm or less especially is desirable in respect of glossiness.

[0043] The particle silica compounded by current and such gaseous-phase method is marketed, and there is various kinds of Aerosil of Japanese Aerosil in a commercial particle silica.

[0044] The colloidal silica preferably used by this invention carries out double decomposition of the specific silicate with an acid etc., or carries out heating aging of the silica gel which is made to pass an ion-exchange-resin layer and is obtained, and is obtained. Using this colloidal silica for an ink jet record form For example, JP,57-14091,A, a 60-219083 official report, A 60-219084 official report, a 61-20792 official report, a 61-188183 official report, A 63-17807 official report, JP,4-93284,A, a 5-278324 official report, A 6-92011 official report, a 6-183134 official report, a 6-297830 official report, It is indicated by a 7-81214 official report, the 7-101142 official report, the 7-179029 official report, the 7-137431 official report, the international patent public presentation WO 94/No. 26530 official report, etc.

[0045] Although the desirable particle diameter of colloidal silica is 5-100nm, its thing with a particle diameter of 7-50nm is usually still more desirable.

[0046] The particle silica and colloidal silica which were compounded by the gaseous-phase method may carry out cation conversion of the front face, for example, may process it by mineral salt, such as aluminum, calcium, Mg, and Ba.

[0047] As for a non-subtlety particle, it is desirable to use in 2-10 by the weight ratio to polyvinyl alcohol, and especially 3-9 are desirable.

[0048] A way acid or its salt is used as a hardening agent.

[0049] A way acid or its salt (it may be hereafter called a hardening agent) is the oxygen acid which uses a boron atom as a neutral atom, and its salt, and, specifically, an altway acid, a meta-way acid, a way [ degree ] acid, tetraboric acid, 5 way acids, and those salts are mentioned.

[0050] You may add in the coating liquid which forms an opening layer, and a hardening agent may be added in the coating liquid which forms the layer of others which adjoin an opening layer. Moreover, after applying the coating liquid which forms the opening layer which does not contain the hardening agent on the base material which has applied the coating liquid which contains a hardening agent beforehand or carrying out spreading desiccation of the coating liquid which forms further the opening layer which does not contain the hardening agent, the overcoat of the hardening agent solution can be carried out, and a hardening agent can be supplied to an opening layer. It is desirable that manufacture adds a hardening agent and forms an opening layer into the coating liquid of the layer which adjoins the coating liquid or this which forms an opening layer, considering an easy point.

[0051] Next, following condition \*\* and condition \*\* which specify this invention are explained.

[0052] Condition \*\*  $0.05 \leq X/Y \leq 0.5$  condition \*\*  $Z/Y \leq 4X$  is the way acid of the per [ unit area ] contained in the ink absorption layer of a record form, or the amount (millimol / m<sup>2</sup>) of the salt.

Y is the amount (millimol / m<sup>2</sup>) of the hydroxyl group per unit area in the polyvinyl alcohol contained in the ink absorption layer of a record form.

Z is the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form when aquosity recording ink is printed by the maximum delivery in a record form (millimol / m<sup>2</sup>).

The way acid of the per [ unit area ] contained in the ink absorption layer of a record form in order to acquire the effectiveness of this invention, or the amount of the salt (millimol / m<sup>2</sup>), When the amount (the millimol / m<sup>2</sup>) and aquosity recording ink of a hydroxyl group per unit area in the polyvinyl alcohol contained in the ink absorption layer of a record form are printed by the maximum delivery in a record form, It is required for three parameters of the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form (millimol / m<sup>2</sup>) to be satisfied with coincidence of the above-mentioned condition \*\* and condition \*\*.

[0053] In this invention, coat degradation at the time of saving on condition that high humidity only after it was satisfied with coincidence of the conditions of the above-mentioned \*\* and \*\* can be prevented.

[0054] It is shown that condition \*\* requires that a ratio with the amount of the amount of hydroxyl groups of polyvinyl alcohol, a way acid, or its salt should be in the specific range. Condition \*\* When the amount of hydroxyl groups and aquosity recording ink of polyvinyl alcohol are printed by the maximum delivery in a record form, it is shown that it is required for a ratio with the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form to be in the specific range.

[0055] Although the reason it must be satisfied with coincidence of a reason in above condition \*\* and condition \*\* does not clarify, in order to give reinforcement sufficient as a coat It is required for the amount of a hardening agent to exist with a moderate ratio to the amount of the hydroxyl group in polyvinyl alcohol. Moreover, since the hydroxyl group of the high-boiling point organic solvent which aquosity recording ink contains reacts to the hydroxyl group and competition target of polyvinyl alcohol with a hardening agent In order to maintain the reaction of a hardening agent and polyvinyl alcohol, the ratio of the amount of hydroxyl groups of the high-boiling point organic solvent which aquosity recording ink contains to the hydroxyl group of polyvinyl alcohol is presumed whether to have importance.

[0056] X, Y, and Z are further explained to a detail below.

[0057] X expresses with millimol / m<sup>2</sup> the way acid of the per [ unit area ] contained in the ink absorption layer of a record form, or the amount of the salt.

[0058] X calculates the value which divided the gram molecule of a way acid or its salt by the number of the boron atoms contained in a way acid or its salt as one mol.

[0059] For example, when orthoboric acid (H<sub>3</sub>BO<sub>3</sub>) or its salt, a meta-way acid (HBO<sub>2</sub>), or its salt converts into per two 1m of record forms and contains 0.01 mols, X is 0.01 (a mol / m<sup>2</sup>) (millimol / m<sup>2</sup>), 10 [ i.e., ]. Moreover, when the tetraboric acid salt (for example, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> grade) which has four boron atoms in 1 molecule converts into per two 1m of record forms and contains 0.01 mols, X is 4x0.01 (a mol / m<sup>2</sup>) (millimol / m<sup>2</sup>), 40 [ i.e., ]. Moreover, when the 5 way acid chloride (for example, NaB<sub>5</sub>O<sub>8</sub> grade) which has five boron atoms in 1 molecule is converted into per two 1m of record forms and is contained 0.01 mols, X is 5x0.01 (a mol / m<sup>2</sup>) (millimol / m<sup>2</sup>), 50 [ i.e., ].

[0060] When two or more way acids or its salts are used together, X is calculated about each, and it is what totaled them and is expressed.

[0061] The molecular weight (=86-0.42xp) (molecular weight of vinyl acetate; 86, molecular-weight;44 of vinyl alcohol) of the appearance of the polyvinyl alcohol of saponification whenever p (%) is used for Y. It is expressed with  $Y=(1000xy) \times (p/100)/(86-0.42xp) = 10xpxy/(86-0.42xp)$  (millimol / m<sup>2</sup>) when the amount of the polyvinyl alcohol converted into per two 1m of record forms is yg.

[0062] For example, it is set to  $Y=10 \times 88 \times 3 / (86-0.42 \times 88) = 53.8$  (millimol / m<sup>2</sup>) when 3g per two of polyvinyl alcohol whenever [ saponification / whose ] is 88% is used 1m of record forms.

[0063] Z expresses the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form with millimol / m<sup>2</sup>, when aquosity recording ink is printed by the maximum delivery in a record form.

[0064] The amount of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form when aquosity recording ink is printed by the maximum delivery in a record form means the amount of the hydroxyl group originating in the high-boiling point organic solvent in the aquosity recording ink contained in per unit area of a record form, when solid printing is carried out by the maximum delivery with the ink jet recording apparatus controlled by printer driver software.

[0065] The organic solvent with which, as for a high-boiling point organic solvent, the boiling point has the boiling point which says an organic solvent 120 degrees C or more, and does not fill this with it is not contained here.

[0066] Generally, in color ink jet record, each ink of black is used together as aquosity recording ink yellow, a Magenta, cyanogen, and if needed, and two or more ink in which color concentration differs in each depending on the case may be used. In such a case, with an ink jet recording apparatus, when solid printing is carried out by the maximum delivery of the combination of various ink according to printer driver software Although the amount of the hydroxyl group which originates in the high-boiling point organic solvent in the aquosity recording ink contained in per unit area of a record form in each combination is calculated When aquosity recording ink is printed by the maximum delivery in a record form, the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form means the greatest thing of the amounts of a \*\*\*\*\* \*\*\*\* hydroxyl group.

[0067] How to ask for Z is concretely explained about the case where three kinds of ink which has the following presentations as aquosity recording ink is used for below.

[0068]

[Table 1]

	Yインク	Mインク	Cインク
染料	2.1g	1.7g	1.9g
DEG	12.0g	8.0g	6.8g
GLY	9.0g	12.0g	15.0g
純水で仕上げ	100 ml	100 ml	100 ml
各 100 ml 中の水酸基の量 (ミリモル)	524	542	617

[0069] DEG: Diethylene glycol ( $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ )

Molecular weight = 106, a number of hydroxyl groups = 2-/mol (molecular weight per hydroxyl group;  $106/2$ )

GLY: Glycerol ( $\text{CH}_2\text{OHCH}(\text{OH})\text{CH}_2\text{OH}$ )

Molecular weight: 92, a number of hydroxyl groups = 3-/mol (molecular weight per hydroxyl group;  $92/3$ )

Front Naka, each ink 100ml — to an inner high-boiling point organic solvent Number [ of the amount Y ink DEG of the originating hydroxyl group ] of hydroxyl groups =  $/(1000 \times 12.0)$  Number [ of =226 millimol GLY ] of hydroxyl groups =  $(106/2) / (1000 \times 9.0)$   $(92/3) = 293$  millimol Y ink 100ml — the number of hydroxyl groups of the amount =of hydroxyl groups  $226 + 298 = 524$  millimol M ink DEG originating in an inner high-boiling point organic solvent — number [ of the =  $(1000 \times 8.0) / (106/2) = 151$  millimol GLY ] of hydroxyl groups = —  $/(1000 \times 12.0)$   $(92/3) = 391$  millimol M ink 100ml — the number of hydroxyl groups of the amount =of hydroxyl groups  $151 + 391 = 542$  millimol C ink DEG originating in an inner high-boiling point organic solvent — number [ of the =  $(1000 \times 6.8) / (106/2) = 128$  millimol GLY ] of hydroxyl groups = — The amount =of hydroxyl groups  $128 + 489 = 617$  millimol ink jet printer originating in an inner high-boiling point organic solvent follows printer driver software.  $(1000 \times 15.0) / (92/3) = 489$  millimol Y ink 100ml — For example, \*\*Y, M, supposing it is printable on the following printing conditions C ink — respectively — independent — solid printing: — it is set to 25ml per two 1m of record forms, respectively — as — the ink of printing \*\*2 color — in piles — printing: — it becomes 50% of independent printing conditions — as — the ink of printing \*\*3 color — in piles — printing: — it becomes 35% of independent printing conditions — as — the conditions more than printing — monochrome solid — 2 color solid — it is as follows, when 3 color solid printing is carried out and the amount of hydroxyl groups per two is calculated 1m.

[0070]

(1) Monochrome solid (the amount of the maximum ink = 25 ml/m<sup>2</sup>)

Y:  $524 \times (25/100) = 131$  millimol M:  $542 \times (25/100) = 136$  millimol C:  $617 \times (25/100) = 154$  millimol (2) 2 color solid (the amount of the maximum ink = 25 ml/m<sup>2</sup>)

Y+M:  $0.5 \times (524 + 542) \times (25/100) = 133$  millimol M+C:  $0.5 \times (542 + 617) \times (25/100) = 145$  millimol C+Y:  $0.5 \times (617 + 524) \times (25/100) = 143$  millimol (3) 3 color solid (the amount of the maximum ink = 26.25 ml/m<sup>2</sup>)

The amounts of hydroxyl groups which originate in the high-boiling point organic solvent which it is a time of carrying out monochrome solid printing of the C ink that the amount of the greatest hydroxyl group is breathed out in this printing condition, and is contained in the aqueosity recording ink at this time from (1) of the  $0.35 \times (524 + 542 + 617) \times (25/100) = 147$  millimol above, (2), and (3) are 154 millimols, and Z is set to 154 millimols / m<sup>2</sup>.

[0071] In this invention, it is desirable that X, Y, and Z fill following condition \*\* and condition \*\*.

[0072] Various kinds of additives can be added in the ink absorption layer of the ink jet record form of condition \*\*  $0.1 \leq X/Y \leq 0.4$  condition \*\*  $Z/Y \leq 3$  this invention.

[0073] Especially, since a cation mordant improves the water resisting property and moisture resistance after printing, it is desirable.

[0074] Although the polymer mordant which has the class [ 1st ] – 3rd class amino group and a quarternary-ammonium-salt radical can be used as a cation mordant, since there being little discoloration by the passage of time and light-fast degradation and the mordanting ability of a color are high enough, the polymer mordant which has a quarternary-ammonium-salt radical is desirable.

[0075] A desirable polymer mordant is the homopolymer of the monomer which has a quarternary-ammonium-salt radical, a copolymer with other monomers, or a condensation polymerization object.

[0076] In the ink absorption layer of the ink jet record form of this invention In addition to a cation mordant, for example, an ultraviolet ray absorbent given in JP,57-74193,A, a 57-87988 official report, and a 62-261476 official report, JP,57-74192,A, a 57-87989 official report, a 60-72785 official report, The fading inhibitor indicated by a 61-146591 official report, JP,1-95091,A, the 3-13376 official report, etc., An anion, a cation or the various surfactants of non-ion, JP,59-42993,A, The fluorescent brightener indicated by a 59-52689 official report, a 62-280069 official report, a 61-242871 official report, JP,4-219266,A, etc., Various well-known additives, such as lubricant, such as a defoaming agent and a diethylene glycol, antiseptics, a thickener, an antistatic agent, and a mat agent, can also be made to contain.

[0077] The ink jet record form kicked to this invention may have the ink absorption layer more than two-layer in



the same base material side. When preparing a two or more layers ink absorption layer, that at least one layer should just be an ink absorption layer of this invention, other layers may be swelling layers which made hydrophilic binders, such as gelatin, the subject, or may be ink absorption layers of this invention.

[0078] In the ink jet record form of this invention, in order to prevent that ink imprints in the prevention to which it adheres at the time of piling up immediately after curl prevention and printing to the opposite side of the side which established ink absorptivity, and other ink jet record forms, it is desirable to prepare the back layer of various classes.

[0079] It changes with the class of base material, thickness, and the configurations and thickness of an ink absorption layer, and although it is not fixed, generally a hydrophilic binder and a hydrophobic binder are used for a back layer. Usually, the thickness of a back layer is chosen in 0.1–10 micrometers.

[0080] Moreover, a back layer can adhere as other record forms, and can split-face-ize a front face to prevention, amelioration of note nature, and a pan for amelioration of the conveyance nature within an ink jet recording device. The organic or inorganic particle whose particle size is 2–20 micrometers can be used for split-face-ization.

[0081] In an ink jet record form, the well-known non-absorptivity base material used for the record form for ink jets can be conventionally used suitably as a non-absorptivity base material. As a non-[ these ] absorptivity base material, for example Polyester system resin, diacetate system resin, The bright film which consists of ingredients, such as thoria TESETO system resin, acrylic resin, polycarbonate system resin, polyvinyl chloride system resin, polyimide system resin, cellophane, and celluloid, Or the resin covering paper which prepared the enveloping layer which becomes at least one side of a base paper from the polyolefin resin which added white pigments etc. (the so-called RC paper), Translucent or the opaque base materials which added white pigments, such as the so-called White pet, are used for polyethylene terephthalate.

[0082] It is desirable to perform corona discharge treatment, undercoating processing, etc. in advance of spreading of an ink absorption layer for the purpose, such as to enlarge bond strength of a base material and an ink absorption layer. Furthermore, the ink jet record forms of this invention may not necessarily be being transparent and colorless and the white and colored record sheet.

[0083] Especially since a record image is close to photograph image quality and the image of high quality is moreover obtained by low cost, the ink jet record form using the paper base material which laminated both sides with polyethylene is desirable.

[0084] Hereafter, the paper base material laminated with polyethylene is explained.

[0085] The stencil paper of a paper base material uses wood pulp as the main raw material, if needed, it adds synthetic fibers, such as synthetic pulps, such as polypropylene, or nylon, and polyester, and paper making is carried out. As wood pulp, although both LBKP, LBSP, NBKP, NBSP LDP and NDP LUKP and NUKP can be used, it is desirable to use more many [ for a staple fiber ] LBKP, NBSP(s), LBSP(s), and NDP(s) and LDP(s). However, it reaches LBSP or the ratio of LDP has 10 % of the weight or more and 70 desirable % of the weight or less.

[0086] Chemical pulp with few impurities (for example, sulfate PARUBU, a sulfite bulb) is desirable, and pulp's is [ the pulp which performed bleaching processing and raised the whiteness degree ] useful.

[0087] Hara Kaminaka can add suitably flexible-ized agents, such as moisture hold-back agents, such as paper reinforcing agents, such as white pigments, such as sizing compounds, such as a higher fatty acid and an alkyl ketene dimer, a calcium carbonate, talc, and titanium oxide, starch, polyacrylamide, and polyvinyl alcohol, a fluorescent brightener, and polyethylene glycols, a dispersant, and the 4th class ammonium, etc.

[0088] The freshness of the pulp used for paper making has desirable 200–500 cc by convention of CSF, and 30 thru/or 70% have the desirable sum of weight % of the 24-mesh residue and weight % of the 42-mesh residue as which the fiber length after beating is specified to JIS-P -8207. In addition, as for weight % of the four-mesh residue, it is desirable that it is 20 or less % of the weight.

[0089] The basis weight of stencil paper has 30 thru/or desirable 250g, and 50 thru/or its 200g are especially desirable. The thickness of stencil paper has 40 thru/or desirable 250 micrometers.

[0090] After a paper-making phase or paper making, calender processing of the stencil paper can be carried out, and it can also give the Takahira slippage. A stencil paper consistency has 0.7 thru/or common 1.2 g/m<sup>2</sup> (JIS-P -8118). Furthermore, stencil paper stiffness has 20 thru/or desirable 200g on the conditions specified to JIS-P -8143.

[0091] A surface sizing compound may be applied to a stencil paper front face, and said sizing compound which can carry out the Hara Kaminaka addition, and the same sizing compound can be used as a surface sizing compound.

[0092] When measured by the hot water extraction method specified by JIS-P -8113, as for pH of stencil paper, it is desirable that it is 5–9.

[0093] although the polyethylene which covers a stencil paper front face and a rear face is mainly the polyethylene (LDPE) of a low consistency, and/or polyethylene (HDPE) of high density — other lines — low

density polyethylene (LLDPE), polypropylene, etc. can be used.

[0094] As for the polyethylene layer by the side of an ink absorption layer, what added the titanium oxide of a rutile or an anatase mold, and improved opacity and a whiteness degree in polyethylene is desirable as widely performed by the printing paper for photographs. The content of titanium oxide is 4 – 13 % of the weight preferably three to 20% of the weight in general to polyethylene.

[0095] in case melting push appearance also of also using as glossy paper is carried out and it coats polyethylene on a stencil paper front face, polyethylene covering paper can form a mat side and a silky surface which perform the so-called mold attachment processing and are obtained with the usual photographic printing paper, and can also be used.

[0096] After preparing an ink absorption layer and a back layer, the amount of the polyethylene used of the front flesh side of stencil paper is chosen so that there may be no curl, damp and when it is saved by highly humid-ization. Usually, let thickness of the polyethylene layer by the side of 20–40 micrometers and a back layer be the range of 10–30 micrometers for the thickness of the polyethylene layer by the side of an ink absorption layer.

[0097] In this invention, the polyethylene covering paper base material which has the following properties can be used preferably.

[0098] A lengthwise direction by the reinforcement specified by :JIS-P -8113 in hauling strength \*\* 2 thru/or 30kg, a longitudinal direction — 20kg\*\* tear: 1 thru/or on the strength — the convention approach by JIS-P -8116 — a lengthwise direction — 10 — or 200g a longitudinal direction — 20 thru/or 200g\*\* compressibility: — two or more 103 Kgf/cm\*\* surface Beck smoothness: — the conditions specified to JIS-P -8119 when using as glossy paper — 20 seconds or more (if the so-called mold attachment article is suited, you may be less than [ this ].)

\*\* Opacity = by the Measuring condition of straight-line light incidence / diffused-light transparency conditions, various configuration layers, such as an under-coating layer prepared especially the configuration layer of the ink jet record form of 15% or less this invention, i.e., if needed [ an ink absorption layer or if needed ] for an opening mold, suitably 20% or less, can be formed using the approach that the transmission in the beam of light of a visible region is well-known. The desirable formation approach is the approach of applying the coating liquid which constitutes each class on a base material, and drying. The coincidence method of application which can also apply more than two-layer to coincidence, and substitutes spreading of all hydrophilic binder layers for one spreading in this case is desirable.

[0099] As the method of application, the extrusion coat method which uses a hopper the roll coating method, a rod bar coating method, the air-knife-coating method, a spray coating method, the curtain method of application, or given in a U.S. Pat. No. 2681294 specification is used preferably.

[0100] Next, when carrying out ink jet record using the ink jet record form of this invention, the aquosity recording ink to be used is explained.

[0101] Aquosity recording ink usually consists of an additive of others which are added water soluble dye, a solvent, and if needed. Although water soluble dye, such as direct dye used by well-known ink jet record as water soluble dye, acid dye, basic dye, reactive dye, or a food dye, can be used, direct dye or acid dye is desirable.

[0102] Although the solvent of aquosity recording ink makes water a subject, when aquosity recording ink dries, a color deposits, and in order to prevent starting blinding in the supply path of a nozzle tip or aquosity recording ink, a high-boiling point organic solvent with the boiling point liquefied above 120 degrees C is added at a room temperature. It is required that it should have vapor pressure [ need / therefore / a high-boiling point organic solvent / to have the operation which formed elements, such as a color, deposit when water evaporates, and prevents generating of a big and rough sludge ] far lower than water. Moreover, the miscibility over water needs to be high.

[0103] As a high-boiling point organic solvent used for such the purpose For example, ethylene glycol, propylene glycol, a diethylene glycol, Triethylene glycol, a glycerol, the diethylene-glycol monomethyl ether, The diethylene-glycol monobutyl ether, the triethylene glycol monobutyl ether, The glycerol monomethyl ether, 1 and 2, 3-butane triol, 1 and 2, 4-butane triol, Alcohols, such as 1, 2, 4-pentanetriol, 1 and 2, 6-hexane triol, thiodiglycol, triethanolamine, and a polyethylene glycol (average molecular weight is about 300 or less), are mentioned. Moreover, dimethylformamide, N-methyl pyrrolidone, etc. can be used also besides having described above.

[0104] Also in the high-boiling point organic solvent of these many, the low-grade alkyl ether of polyhydric alcohol, such as polyhydric alcohol, such as a diethylene glycol, triethanolamine, and a glycerol, triethanolamine, and the triethylene glycol monobutyl ether, etc. is desirable.

[0105] As an additive of others which are added by aquosity recording ink if needed, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rusr-proofer, etc. are mentioned, for example.

[0106] Aquosity recording ink is the purpose which wettability to a record form is made [ purpose ] good, or

stabilizes the regurgitation from an ink jet nozzle, and it is desirable in 25 degrees C to have the surface tension of 28 – 40 dyne/cm within the limits preferably 25 to 50 dyne/cm.

[0107] Moreover, in 25 degrees C, 2–10Cp is desirable still more desirable, and the viscosity of aqueous recording ink is usually 2.5–8Cp. Moreover, when the capacity of the liquid ink drop by which 3–9 are breathed out from a desirable ink nozzle is 1–30pL, since the diameter of a dot with a diameter of about 20–60 micrometers is obtained in the record paper, pH of aqueous recording ink is desirable. The color-print printed with such a diameter of a dot gives a high-definition image. Furthermore, the capacity of the desirable minimum liquid ink drop is 2–20pL.

[0108] Moreover, when concentration carries out ink jet record about a Magenta and cyanogen at least by the recording method using the aqueous recording ink which is two kinds different more than twice, since low-concentration ink is used, it is hard coming to carry out discernment of a dot in the highlights section, but this invention can be used also when this recording method is used.

[0109] In the ink jet record approach, various kinds of well-known methods can be conventionally used as the record approach. The detail of the record approach is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

[0110]

[Example] This invention is not limited by these examples although an example explains this invention concretely below.

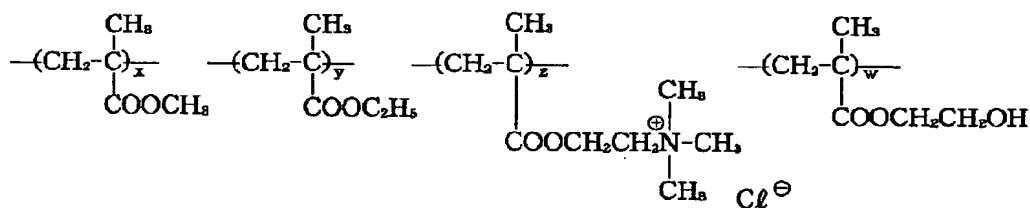
[0111] The paper base material which covered both sides of the stencil paper for photographs of example 1160 g/m<sup>2</sup> with polyethylene (the polyethylene layer which contains an anatase mold titanium dioxide with a thickness of 35 micrometers 13% of the weight should be formed in the recording surface side, and as for thickness, a polyethylene layer should be formed in a rear-face side by 25 micrometers, and let Tg=65 degree C acrylic latex resin be solid content on it) The back layer in which 0.6 g/m<sup>2</sup> and a mean diameter make a mat agent the silica which is about 13 micrometers, and contain it two times 0.3 g/m is formed. It prepared.

[0112] Next, in 900ml of pure water, it added, while the mean diameter of a primary particle agitated 180g of particle silica powder which is about 7nm with the high-speed homogenizer, and the silica water dispersion was produced. Next, in this silica water dispersion, 120ml of 20% water solutions of the following cationic mordant was added, the high-speed homogenizer distributed for 30 minutes, and pale clear dispersion liquid were obtained. Next, average degree of polymerization added gradually 400ml (ethyl acetate is contained 4% of the weight) of 5% polyvinyl alcohol water solutions whenever [ saponification / whose ] is 88% by 3500. Subsequently, the amount which shows a borated water solution (20% ethanol content) in Table 1 5% as a hardening agent was added, and further, after adding 50ml of gelatin water solutions 10%, the coating liquid which makes 2100ml to the whole quantity with pure water, and forms an opening layer was produced.

[0113]

[Formula 1]

カチオン性媒染剤



$$x : y : z : w = 25 : 25 : 45 : 5 \text{ (モル比)}$$

$$\text{平均分子量} \approx 23,000$$

[0114] Subsequently, the coating liquid obtained as mentioned above was warmed at 40 degrees C, it applied so that humid thickness might be set to 220 micrometers at the recording surface side of the paper base material covered with the above-mentioned polyethylene, and it was made to cool so that spreading coat temperature may become 15 degrees C or less (for 20 seconds). Subsequently, the 40-degree C wind was sprayed for the 30-degree C wind for 60 seconds for 60 seconds, for 120 seconds and a 35 more-degree C wind were sprayed for 60 seconds and for a 45-degree C wind one by one for 60 seconds, the 25-degree C wind was dried, further, 25 degrees C and the ambient atmosphere of 50% of relative humidity were passed for 120 seconds, gas conditioning was carried out, and the record forms 1–5 were produced.

[0115] In the above-mentioned record forms 1–5, average degree of polymerization produced similarly the record forms 16–20 set to the record forms 11–15 used as 6–10,600ml of record forms which set to 500ml the amount of 5% polyvinyl alcohol water solution whenever [ saponification / whose ] is 88%, and 800ml by 3500.

[0116] The obtained record forms 1–20 were saved for three days at 35 degrees C.

[0117] Next, the aqueosity recording ink for ink jets was prepared as follows.

[Yellow ink -1]

Direct yellow 86 2.0g Diethylene glycol 22.2g Glycerol 4.5g 100ml is made with pure water.

[Magenta ink -1]

Direct red 227 1.8g Glycerol 3.5g Diethylene-glycol monobutyl ether 21.5g 100ml is made with pure water.

[Cyanogen INKU 1]

Direct blue 199 2.4g Ethylene glycol 16.1g Glycerol 9.5g 100ml is made with pure water.

[0118] The number of hydroxyl groups per 100ml of each above-mentioned aqueosity recording ink for ink jets is as follows.

[yellow ink -1] — :566 millimol — /100ml [Magenta INKU 1]:247 millimol / 100ml [cyanogen ink -1]:829 millimol / 100ml, next an ink jet — service water — it printed in the record forms 1-20 using sex recording ink with the on-demand mold ink jet printer (drop capacity =25pL, maximum print density =720dpix720dpi). Printing was performed by monochrome solid, 2 color solid, and 3 color solid printing, respectively.

[0119] When printing, monochrome solid printing was performed with the maximum print density (the amount of ink = 20ml/m<sup>2</sup>), respectively, and, as for 2 color printing, 3 color solid performed each color with 40% of the maximum print density (the amount of ink = 24 ml/m<sup>2</sup>) 60% of the maximum print density (the amount of ink = 24 ml/m<sup>2</sup>).

[0120] The amount of the hydroxyl group originating in the high-boiling point organic solvent in each solid section at this time is as being shown in Table 2 (millimol / m<sup>2</sup>).

[0121]

[Table 2]

単色ベタ			2色ベタ			3色ベタ
Y	M	C	Y+M	M+C	C+Y	Y+M+C
113	49	166	98	129	167	131

[0122] Z (the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form when aqueosity recording ink is printed by the maximum delivery in a record form) in the above-mentioned printing conditions of Table 2 to this aqueosity recording ink is 167 millimols / m<sup>2</sup>.

[0123] The printed record forms 1-20 were saved for two days at 40 degrees C and 80% of relative humidity. The crack situation of the film surface of the saved sample was visually checked using the magnifier, and the following valuation bases estimated.

a <valuation basis> — O: — although it can check with O:magnifier which the crack has not generated even if it checks with a magnifier, it turns out that the intense crack has occurred in x:viewing understood that the crack has occurred slightly in \*\*:viewing which the crack which cannot be distinguished only visually has generated.

[0124] The obtained result was shown in Table 3.

[0125]

[Table 3]

記録用紙No.	ほう酸		PVAの 水酸基数 (Y)	$\frac{X}{Y}$	$\frac{Z}{Y}$	保存後ひび割れ							
	m l	X				Y	M	C	Y + M	M + C	C + Y	Y + M + C	
1	比較例	30	2.5	37.6	0.066	4.44	△	○	×	○	△	×	△
2	比較例	60	5.1	37.6	0.136	4.44	○	◎	×	◎	○	×	○
3	比較例	90	7.6	37.6	0.202	4.44	○	◎	×	◎	○	×	○
4	比較例	150	12.7	37.6	0.338	4.44	○	○	×	○	○	×	○
5	比較例	300	25.3	37.6	0.672	4.44	△	○	×	×	△	×	△
6	本発明	30	2.5	47.0	0.053	3.55	△	○	△	◎	○	△	○
7	本発明	60	5.1	47.0	0.109	3.55	◎	◎	○	◎	◎	○	◎
8	本発明	90	7.6	47.0	0.162	3.55	◎	◎	○	◎	◎	○	◎
9	本発明	150	12.7	47.0	0.270	3.55	◎	◎	○	◎	◎	○	◎
10	比較例	300	25.3	47.0	0.538	3.55	○	◎	×	△	○	×	○
11	比較例	30	2.5	56.4	0.044	2.98	△	○	×	△	○	×	○
12	本発明	60	5.1	56.4	0.091	2.98	○	◎	○	○	○	○	○
13	本発明	90	7.6	56.4	0.136	2.98	◎	◎	◎	◎	◎	◎	◎
14	本発明	150	12.7	56.4	0.226	2.98	◎	◎	◎	◎	◎	◎	◎
15	本発明	300	25.3	56.4	0.452	2.98	◎	◎	○	◎	◎	○	◎
16	比較例	30	2.5	75.2	0.033	2.23	△	○	×	○	○	×	○
17	本発明	60	5.1	75.2	0.068	2.23	◎	◎	○	◎	◎	○	◎
18	本発明	90	7.6	75.2	0.101	2.23	◎	◎	◎	◎	◎	◎	◎
19	本発明	150	12.7	75.2	0.169	2.23	◎	◎	◎	◎	◎	◎	◎
20	本発明	300	25.3	75.2	0.337	2.23	◎	◎	◎	◎	◎	◎	◎

[0126] The result of Table 3 shows that a crack does not arise in the solid printing section even if saved under an elevated temperature and highly humid when satisfying both condition \*\*s and condition \*\*s of this invention.

[0127] Especially, when  $X/Y$  is 0.4 or less [ 0.1 or more ] and  $Z/Y$  is three or less, it turns out that there are few cracks.

[0128] The aquosity recording ink for example 2 ink jets was prepared as follows.

[Yellow INKU 2]

Direct yellow 86 2.0g diethylene glycol 21.5g glycerol 100ml is made with 9.8g pure water.

[Magenta ink -2]

Direct red 227 1.8g glycerol 10.5g diethylene glycol 100ml is made with 19.5g pure water.

[Cyanogen ink -2]

Direct blue 199 2.4g ethylene glycol 16.1g glycerol 100ml is made with 12.9g pure water.

[0129] The number of hydroxyl groups per 100ml of each above-mentioned aquosity recording ink for ink jets is as follows.

[yellow ink -1] — :725 millimol / 100ml [Magenta ink -1] — the on-demand mold ink jet printer used in :710 millimol / 100ml [cyanogen ink -1]:940 millimol / the 100ml example 1 — using — printing conditions given in an example 1 — monochrome solid and 2 color solid — 3 color solid printing was carried out.

[0130] The amount of the hydroxyl group originating in the high-boiling point organic solvent in each solid section at this time is as being shown in Table 4 (millimol / m2).

[0131]

[Table 4]

単色ベタ			2色ベタ			3色ベタ
Y	M	C	Y+M	M+C	C+Y	Y+M+C
145	142	188	172	198	200	190

[0132] Z (the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form when aquosity recording ink is printed by the maximum delivery in a record form) in the above-mentioned printing conditions of Table 4 to this aquosity recording ink is 200 millimols / m2.

[0133] Subsequently, the crack situation of a film surface as well as an example 1 was evaluated about the record forms 1-20 obtained by printing.

[0134] The obtained result is shown in Table 5.

[0135]

[Table 5]

記録用紙No.		ほう酸		PVAの 水酸基数 (Y)	$\frac{X}{Y}$	$\frac{Z}{Y}$	保存後ひび割れ						
		mℓ	X				Y	M	C	Y + M	M + C	C + Y	Y + M + C
1	比較例	30	2.5	37.6	0.066	5.32	×	×	×	×	×	×	×
2	比較例	60	5.1	37.6	0.136	5.32	△	△	×	×	×	×	×
3	比較例	90	7.6	37.6	0.202	5.32	△	△	×	×	×	×	×
4	比較例	150	12.7	37.6	0.338	5.32	○	○	×	×	×	×	×
5	比較例	300	25.3	37.6	0.672	5.32	△	△	×	×	×	×	×
6	比較例	30	2.5	47.0	0.053	4.25	×	×	×	×	×	×	×
7	比較例	60	5.1	47.0	0.109	4.25	○	○	×	×	×	×	×
8	比較例	90	7.6	47.0	0.162	4.25	○	○	△	△	×	×	×
9	比較例	150	12.7	47.0	0.270	4.25	○	○	△	△	×	×	×
10	比較例	300	25.3	47.0	0.538	4.25	△	△	×	×	×	×	×
11	比較例	30	2.5	56.4	0.044	3.55	×	×	×	×	×	×	×
12	本発明	60	5.1	56.4	0.091	3.55	○	○	○	○	○	○	○
13	本発明	90	7.6	56.4	0.136	3.55	◎	◎	○	○	○	○	○
14	本発明	150	12.7	56.4	0.226	3.55	◎	◎	○	○	○	○	○
15	本発明	300	25.3	56.4	0.452	3.55	○	○	○	○	○	○	○
16	比較例	30	2.5	75.2	0.033	2.67	×	×	×	×	×	×	×
17	本発明	60	5.1	75.2	0.068	2.67	◎	◎	○	○	○	○	○
18	本発明	90	7.6	75.2	0.101	2.67	◎	◎	◎	◎	◎	◎	◎
19	本発明	150	12.7	75.2	0.169	2.67	◎	◎	◎	◎	◎	◎	◎
20	本発明	300	25.3	75.2	0.337	2.67	◎	◎	◎	◎	◎	◎	◎

[0136] When satisfying both condition \*\*s and condition \*\*s of this invention like an example 1 from the result of Table 5, it turns out whether even if it saves all under an elevated temperature and highly humid, the crack has hardly arisen, and that it is not generated at all.

[0137]

[Effect of the Invention] According to the ink jet record approach of this invention, even if saved under high-humidity/temperature, the printing record which does not produce a crack can be acquired.

[Translation done.]

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**TECHNICAL FIELD**

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[Industrial Application] This invention relates to the ink jet record approach performed in more detail using the ink jet record form which prevented degradation of the coat after printing, and which has the ink absorption layer of the opening mold which has high ink absorptivity about the ink jet record approach which records on an ink jet record form by using water color ink.

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**PRIOR ART**

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[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-color-izing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, amelioration progresses from both sides of ink and equipment, and it has spread quickly in various fields, such as various printers, facsimile, and a computer terminal, current.

[0003] The detail is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

[0004] As an ink jet record form, various record forms are used from the former. For example, the ink jet record form which painted the ink absorption layer as a record layer on the base material which consists of a regular paper, a hydrophilic binder and various kinds of coated paper which painted the layer which consists of an inorganic pigment (art paper, coat paper, cast coated paper, etc.), various kinds of papers that covered both sides with plastic resin, transparence, or various kinds of opaque plastic film is used further.

[0005] The above-mentioned ink absorption layer is roughly divided into the ink absorption layer of the opening mold which prepared the opening into the ink absorption layer of the swelling mold constituted by the subject in the hydrophilic binder, and the record layer.

[0006] The ink absorption layer of an opening mold holds ink to the opening formed in the layer, and the opening is formed by making various kinds of inorganic solid-state particles and organic solid-state particles contain in a coat.

[0007] As an ink jet record form, when a printing dot laps [ that the concentration of a printing dot is high and a color tone is brightly skillful, and absorption of ink ] early, ink flows out or it spreads, or the diffusion to the longitudinal direction of not carrying out and a printing dot is not large beyond the need, and engine performance, such as the circumference being smooth and not fading, is required.

[0008] when the ink rate of absorption of an ink absorption layer is slow, in case the liquid ink drop of two or more colors laps and is recorded, the color of each other in the border area of a color which the drop of ink causes a HAJIKI phenomenon on a record form, and produces nonuniformity and is different is \*\*\*\* — since it \*\* and image quality is reduced greatly, it is required that high ink absorptivity should be given to an ink jet record form.

[0009] In order to solve these problems For example, the record form which carried out humidity of the coating for surface treatment to the low size stencil paper indicated by JP,52-53012,A, The record form which prepared the coated layer of ink absorptivity in the support surface indicated by JP,55-5830,A, The record form which contains non-colloid silica powder as a pigment in the enveloping layer indicated by JP,56-157,A, The record form which used together the inorganic pigment indicated by JP,57-107878,A and the organic pigment, The record form which has two hole distribution peaks indicated by JP,58-110287,A, The record form which consists of a vertical two-layer porous layer indicated by JP,62-111782,A, The record form which has the indeterminate form crack indicated by JP,59-68292,A, the 59-123696 official report, the 60-18383 official report, etc., The record form which has the fines non-layer indicated by JP,61-135786,A, the 61-148092 official report, the 62-149475 official report, etc., JP,63-252779,A, JP,1-108083,A, The record form containing the pigment which has the specific physical-properties value indicated by the 2-136279 official report, the 3-65376 official report, the 3-27976 official report, etc., or a particle silica, JP,57-14091,A, a 60-219083 official report, a 60-210984 official report, A 61-20797 official report, a 61-188183 official report, JP,5-278324,A, The record form containing particle silicas, such as a colloid silica indicated by the 6-92011 official report, the 6-183134 official report, the 7-137431 official report, the 7-276789 official report, etc., And JP,2-276671,A, a 3-67684 official report, a 3-215082 official report, Very many techniques, such as a record form containing the hydrated alumina particle indicated by the 3-251488 official report, the 4-67986 official report, the 4-263983 official report, the 5-16517 official report, etc., are proposed.

[0010] In an ink jet record form, although it is desirable if it has a high absorption capacity and ink absorptivity and carries out from a viewpoint of absorption of ink when absorptivity is in the base material itself, there is a



problem of a base material lenticulating, and Siwa being generated on an image or being [ a color permeates partially into a base material and ] hard to come after ink jet record out of concentration.

[0011] Although the above-mentioned fault was not generated but the clear image with high concentration was obtained when a base material was non-absorptivity, there was a problem that the amount of the opening which absorbs the ink formed into an ink absorption layer received a limit.

[0012] For example, in the ink absorption layer whose desiccation thickness is 40 micrometers, although there will be only the amounts of openings of only 18 ml/m<sup>2</sup> per two 1m of ink jet record forms and it will be based also on a recording method if it is \*\*\*\*\* in which solid content can form a coat with a thickness of 22 micrometers, the case where the capacity of the opening which absorbs ink near the amount of the maximum ink runs short may arise.

[0013] If spreading thickness is increased, high void volume will be obtained, but if spreading thickness is increased, a coat will become brittle and the problem that a crack arises under low humidity or the adhesive property over a base material falls will arise.

[0014] These people proposed the approach of improving the film formation nature of a coat, and brittleness, by adding the hydrophilic binder which forms opening structure, and the hardening agent which can construct a bridge, in order to solve the above-mentioned trouble. (Japanese Patent Application No. No. 283636 [ eight to ])

The ink jet record form of the opening mold which used polyvinyl alcohol as a hydrophilic binder, used a way acid or its salt as a hardening agent, and formed the ink absorption layer of an opening mold is especially desirable as an ink jet record form.

[0015] However, when ink jet record was carried out to the ink jet record form which has the ink absorption layer were using polyvinyl alcohol as the above-mentioned hydrophilic binder, and using a way acid or its salt as a hardening agent by the water color ink which contains the compound which has a hydroxyl group as a high-boiling point organic solvent and the recorded form was saved under an elevated temperature and highly humid, it became clear that the problem which a crack produces in a coat arose partially.

[0016] When many things were examined about this cause, it became clear that it was for a coat to deteriorate according to an operation of the compound containing the hydroxyl group contained in aquosity recording ink.

[0017] Moreover, when the content of the non-subtlety particle used in order that this crack may form an opening is less than two in a weight ratio to polyvinyl alcohol, in order to form an opening, considering hardly generating, it is presumed that the non-subtlety particle used so much is for reducing the film formation nature of the polyvinyl alcohol in the printing section.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] According to the ink jet record approach of this invention, even if saved under high-humidity/temperature, the printing record which does not produce a crack can be acquired.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] It is made in view of the above-mentioned actual condition, and this invention is the purpose of this invention, When ink jet record is carried out to the ink jet record form which has the ink absorption layer were using polyvinyl alcohol as the above-mentioned hydrophilic binder, and using a way acid or its salt as a hardening agent with the aquosity recording ink which contains the compound which has a hydroxyl group as a high-boiling point organic solvent, even if it saves the recorded form under high-humidity/temperature, it is in offering the ink jet record approach which does not produce a crack.

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## MEANS

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[Means for Solving the Problem] The above-mentioned technical problem in the ink absorption layer on a non-absorptivity base material Polyvinyl alcohol, In the ink jet record approach which records the compound which uses an ink jet recording device for the ink jet record form containing a non-subtlety particle and a way acid, or its salt, and has a hydroxyl group with the aquosity recording ink contained as a high-boiling point organic solvent The way acid of the per [ unit area ] contained in the ink absorption layer of a record form, or the amount of the salt, When the amount of the hydroxyl group per unit area in the polyvinyl alcohol contained in the ink absorption layer of a record form and aquosity recording ink are printed by the maximum delivery in a record form, The ink jet record approach characterized by making the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form into the amount which is satisfied with coincidence of following condition \*\* and condition \*\*.

[0020] condition \*\* — the way acid of the per [ unit area ] by which X is contained in the ink absorption layer of a record form among  $0.05 \leq X/Y \leq 0.5$  condition \*\*  $Z/Y \leq 4$  type, or the amount (millimol / m<sup>2</sup>) of the salt Y is the amount (millimol / m<sup>2</sup>) of the hydroxyl group per unit area in the polyvinyl alcohol contained in the ink absorption layer of a record form.

Z is the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form when aquosity recording ink is printed by the maximum delivery in a record form (millimol / m<sup>2</sup>).

\*\*\*\*\*.

[0021] This invention is explained to a detail below.

[0022] The ink jet record form used for this invention has the ink absorption layer (it may be hereafter called an opening layer) of an opening mold on a non-absorptivity base material.

[0023] In this invention, since voidage high in an opening layer is obtained, polyvinyl alcohol is used as a hydrophilic binder. Since an interaction is considered as a non-subtlety particle and it is easy to form flocculation, polyvinyl alcohol can form an opening efficiently.

[0024] Cation denaturation polyvinyl alcohol, Nonion denaturation polyvinyl alcohol, and anion denaturation polyvinyl alcohol are also contained in the polyvinyl alcohol as used in the field of this invention.

[0025] Considering the viewpoint which improves film formation nature, the average degree of polymerization of polyvinyl alcohol has that desirable of 1000–5000, and 2000 especially or more are desirable.

[0026] Whenever [ saponification / of polyvinyl alcohol ] has 70 – 100% of desirable thing, and 80 – 100% of especially its thing is desirable.

[0027] Cation conversion polyvinyl alcohol is polyvinyl alcohol which has the 1–3rd class amino group which is indicated by JP,61–10483,A, and the 4th class ammonium in the main \*\* of polyvinyl alcohol, or a side chain, and it is obtained by saponifying the copolymer of the ethylenic unsaturated monomer and vinyl acetate which have a cationic radical.

[0028] As an ethylenic unsaturated monomer which has a cationic radical For example, TORIMECHIRU–(2–acrylamide –2, 2–dimethyl ethyl) ammoniumchloride, TORIMECHIRU–(3–acrylamide –3, 3–dimethyl propyl) ammoniumchloride, N–vinyl imidazole, N–vinyl–2–methyimidazole, N–(3–dimethylaminopropyl) methacrylamide, Hydroxyl ethyl trimethylammonium chloride, TORIMECHIRU–(methacrylamide propyl) ammoniumchloride, N–(1 and 1–dimethyl–3–dimethylaminopropyl) acrylamide, etc. are mentioned.

[0029] the copolymer of the ethylenic unsaturated monomer and vinyl acetate which have a cationic radical — setting — the ratio of a cation denaturation radical content monomer — vinyl acetate — receiving — 0.1–10–mol % — it is 0.2–5–mol % preferably.

[0030] The copolymer of vinyl alcohol which is indicated by the polyvinyl alcohol and JP,61–237681,A which have an anionic radical which is indicated by JP,1–206088,A as anion denaturation polyvinyl alcohol, for example, and the 63–307979 official report, and the vinyl compound which has a water-soluble radical, and the denaturation polyvinyl alcohol which has a water-soluble radical which is indicated by JP,7–285265,A are mentioned.

[0031] The polyvinyl alcohol derivative which added a polyalkylene oxide radical which is indicated by JP,7–9758,A to a part of vinyl alcohol as Nonion denaturation polyvinyl alcohol, for example, and the block copolymer

of the vinyl compound and vinyl alcohol which have the hydrophobic radical indicated by JP,8-25795,A are mentioned.

[0032] Other hydrophilic binders can be made to contain with polyvinyl alcohol in an opening layer. As for other hydrophilic binders, it is desirable that it is 20 or less % of the weight in general to polyvinyl alcohol.

[0033] In this invention, the non-subtlety particle is used in order to form an opening in an ink absorption layer.

[0034] As a non-subtlety particle, white inorganic pigments, such as precipitated calcium carbonate, whiting, a magnesium carbonate, a kaolin, clay, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc hydroxide, zinc sulfide, zinc carbonate, a hydrotalcite, aluminum silicate, the diatom earth, a calcium silicate, a magnesium silicate, synthetic amorphous silica, colloidal silica, an alumina, a colloidal alumina, pseudo-boehmite, an aluminum hydroxide, a lithopone, a zeolite, and a magnesium hydroxide, etc. can be mentioned, for example.

[0035] Homogeneity may distribute in the binder with the primary particle, and a non-subtlety particle forms secondary floc and may be distributed by homogeneity in the binder.

[0036] As for a non-subtlety particle, it is desirable from an glossy viewpoint that the particle size of a primary particle uses a thing 30nm or less.

[0037] When the mean diameter of a primary particle uses the non-subtlety particle exceeding 30nm and the water-soluble polymer mordant of a cation mold is used as a mordant, floc which the water-soluble polymer mordant of a cation mold and condensation become easy to take place, and formed will also be made big and rough more, and glossiness will fall. Especially the particle size of a desirable primary particle is 20nm or less.

[0038] Especially although especially the minimum of the particle size of a primary particle is not limited, 3nm or more is 6nm or more in general from the viewpoint on manufacture of a particle.

[0039] The mean particle diameter of a non-subtlety particle observes the particle which appeared in the cross section and front face of the particle itself or an opening layer with an electron microscope, and is called for as the arithmetic average value (individual number average) in quest of the particle size of the particle of 100 arbitration. The particle size of the particle of each [ here ] is expressed with the diameter when assuming a circle equal to the projected area.

[0040] As an inorganic particle, it is desirable that it makes the ratio of the non-subtlety particle which exceeds 50nm in this case 50 or less % of the weight to all inorganic particles although the mean particle diameter of a primary particle is possible also for the non-subtlety particle and mean particle diameter of 50nm or less using together a non-subtlety particle 50nm or more, and 20 or less % of the weight is more desirable.

[0041] Considering the point of that a clear image is recordable, being able to manufacture by low cost that an image with high concentration is formed, as a non-subtlety particle, it is desirable to use the non-subtlety particle chosen from the particle silica and colloidal silica which were compounded by the gaseous-phase method, and it is most desirable to use the silica compounded by the gaseous-phase method.

[0042] The particle silica compounded by the gaseous-phase method can burn and obtain a silicon tetrachloride at an elevated temperature with hydrogen and oxygen, and is usually silica powder whose particle diameter of a primary particle is 5-500nm. What has the primary particle diameter of 30nm or less especially is desirable in respect of glossiness.

[0043] The particle silica compounded by current and such gaseous-phase method is marketed, and there is various kinds of Aerosil of Japanese Aerosil in a commercial particle silica.

[0044] The colloidal silica preferably used by this invention carries out double decomposition of the specific silicate with an acid etc., or carries out heating aging of the silica gel which is made to pass an ion-exchange-resin layer and is obtained, and is obtained. Using this colloidal silica for an ink jet record form For example, JP,57-14091,A, a 60-219083 official report, A 60-219084 official report, a 61-20792 official report, a 61-188183 official report, A 63-17807 official report, JP,4-93284,A, a 5-278324 official report, A 6-92011 official report, a 6-183134 official report, a 6-297830 official report, It is indicated by a 7-81214 official report, the 7-101142 official report, the 7-179029 official report, the 7-137431 official report, the international patent public presentation WO 94/No. 26530 official report, etc.

[0045] Although the desirable particle diameter of colloidal silica is 5-100nm, its thing with a particle diameter of 7-50nm is usually still more desirable.

[0046] The particle silica and colloidal silica which were compounded by the gaseous-phase method may carry out cation conversion of the front face, for example, may process it by mineral salt, such as aluminum, calcium, Mg, and Ba.

[0047] As for a non-subtlety particle, it is desirable to use in 2-10 by the weight ratio to polyvinyl alcohol, and especially 3-9 are desirable.

[0048] A way acid or its salt is used as a hardening agent.

[0049] A way acid or its salt (it may be hereafter called a hardening agent) is the oxygen acid which uses a boron atom as a neutral atom, and its salt, and, specifically, an alt.way acid, a meta-way acid, a way [ degree ] acid, tetraboric acid, 5 way acids, and those salts are mentioned.

[0050] You may add in the coating liquid which forms an opening layer, and a hardening agent may be added in

the coating liquid which forms the layer of others which adjoin an opening layer. Moreover, after applying the coating liquid which forms the opening layer which does not contain the hardening agent on the base material which has applied the coating liquid which contains a hardening agent beforehand or carrying out spreading desiccation of the coating liquid which forms further the opening layer which does not contain the hardening agent, the overcoat of the hardening agent solution can be carried out, and a hardening agent can be supplied to an opening layer. It is desirable that manufacture adds a hardening agent and forms an opening layer into the coating liquid of the layer which adjoins the coating liquid or this which forms an opening layer, considering an easy point.

[0051] Next, following condition \*\* and condition \*\* which specify this invention are explained.

[0052] Condition \*\*  $0.05 \leq X/Y \leq 0.5$  condition \*\*  $Z/Y \leq 4X$  is the way acid of the per [ unit area ] contained in the ink absorption layer of a record form, or the amount (millimol / m<sup>2</sup>) of the salt.

Y is the amount (millimol / m<sup>2</sup>) of the hydroxyl group per unit area in the polyvinyl alcohol contained in the ink absorption layer of a record form.

Z is the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form when aqueosity recording ink is printed by the maximum delivery in a record form (millimol / m<sup>2</sup>).

The way acid of the per [ unit area ] contained in the ink absorption layer of a record form in order to acquire the effectiveness of this invention, or the amount of the salt (millimol / m<sup>2</sup>), When the amount (the millimol / m<sup>2</sup>) and aqueosity recording ink of a hydroxyl group per unit area in the polyvinyl alcohol contained in the ink absorption layer of a record form are printed by the maximum delivery in a record form, It is required for three parameters of the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form (millimol / m<sup>2</sup>) to be satisfied with coincidence of the above-mentioned condition \*\* and condition \*\*.

[0053] In this invention, coat degradation at the time of saving on condition that high humidity only after it was satisfied with coincidence of the conditions of the above-mentioned \*\* and \*\* can be prevented.

[0054] It is shown that condition \*\* requires that a ratio with the amount of the amount of hydroxyl groups of polyvinyl alcohol, a way acid, or its salt should be in the specific range. Condition \*\* When the amount of hydroxyl groups and aqueosity recording ink of polyvinyl alcohol are printed by the maximum delivery in a record form, it is shown that it is required for a ratio with the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form to be in the specific range.

[0055] Although the reason it must be satisfied with coincidence of a reason in above condition \*\* and condition \*\* does not clarify, in order to give reinforcement sufficient as a coat It is required for the amount of a hardening agent to exist with a moderate ratio to the amount of the hydroxyl group in polyvinyl alcohol. Moreover, since the hydroxyl group of the high-boiling point organic solvent which aqueosity recording ink contains reacts to the hydroxyl group and competition target of polyvinyl alcohol with a hardening agent In order to maintain the reaction of a hardening agent and polyvinyl alcohol, the ratio of the amount of hydroxyl groups of the high-boiling point organic solvent which aqueosity recording ink contains to the hydroxyl group of polyvinyl alcohol is presumed whether to have importance.

[0056] X, Y, and Z are further explained to a detail below.

[0057] X expresses with millimol / m<sup>2</sup> the way acid of the per [ unit area ] contained in the ink absorption layer of a record form, or the amount of the salt.

[0058] X calculates the value which divided the gram molecule of a way acid or its salt by the number of the boron atoms contained in a way acid or its salt as one mol.

[0059] For example, when orthoboric acid (H<sub>3</sub>BO<sub>3</sub>) or its salt, a meta-way acid (HBO<sub>2</sub>), or its salt converts into per two 1m of record forms and contains 0.01 mols, X is 0.01 (a mol / m<sup>2</sup>) (millimol / m<sup>2</sup>), 10 [ i.e., ]. Moreover, when the tetraboric acid salt (for example, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> grade) which has four boron atoms in 1 molecule converts into per two 1m of record forms and contains 0.01 mols, X is 4x0.01 (a mol / m<sup>2</sup>) (millimol / m<sup>2</sup>), 40 [ i.e., ]. Moreover, when the 5 way acid chloride (for example, NaB<sub>5</sub>O<sub>8</sub> grade) which has five boron atoms in 1 molecule is converted into per two 1m of record forms and is contained 0.01 mols, X is 5x0.01 (a mol / m<sup>2</sup>) (millimol / m<sup>2</sup>), 50 [ i.e., ].

[0060] When two or more way acids or its salts are used together, X is calculated about each, and it is what totaled them and is expressed.

[0061] The molecular weight (=86-0.42xp) (molecular weight of vinyl acetate; 86, molecular-weight;44 of vinyl alcohol) of the appearance of the polyvinyl alcohol of saponification whenever p (%) is used for Y. It is expressed with  $Y = (1000xy) \times (p/100) / (86 - 0.42xp) = 10xpxy / (86 - 0.42xp)$  (millimol / m<sup>2</sup>) when the amount of the polyvinyl alcohol converted into per two 1m of record forms is yg.

[0062] For example, it is set to  $Y = 10 \times 88 \times 3 / (86 - 0.42 \times 88) = 53.8$  (millimol / m<sup>2</sup>) when 3g per two of polyvinyl alcohol whenever [ saponification / whose ] is 88% is used 1m of record forms.

[0063] Z expresses the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form with millimol / m<sup>2</sup>, when aquosity recording ink is printed by the maximum delivery in a record form.

[0064] The amount of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form when aquosity recording ink is printed by the maximum delivery in a record form means the amount of the hydroxyl group originating in the high-boiling point organic solvent in the aquosity recording ink contained in per unit area of a record form, when solid printing is carried out by the maximum delivery with the ink jet recording apparatus controlled by printer driver software.

[0065] The organic solvent with which, as for a high-boiling point organic solvent, the boiling point has the boiling point which says an organic solvent 120 degrees C or more, and does not fill this with it is not contained here.

[0066] Generally, in color ink jet record, each ink of black is used together as aquosity recording ink yellow, a Magenta, cyanogen, and if needed, and two or more ink in which color concentration differs in each depending on the case may be used. In such a case, with an ink jet recording apparatus, when solid printing is carried out by the maximum delivery of the combination of various ink according to printer driver software Although the amount of the hydroxyl group which originates in the high-boiling point organic solvent in the aquosity recording ink contained in per unit area of a record form in each combination is calculated When aquosity recording ink is printed by the maximum delivery in a record form, the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form means the greatest thing of the amounts of a \*\*\*\*\* \*\*\*\* hydroxyl group.

[0067] How to ask for Z is concretely explained about the case where three kinds of ink which has the following presentations as aquosity recording ink is used for below.

[0068]

[Table 1]

	Yインク	Mインク	Cインク
染料	2.1g	1.7g	1.9g
DEG	12.0g	8.0g	6.8g
GLY	9.0g	12.0g	15.0g
純水で仕上げ	100 ml	100 ml	100 ml
各 100ml 中の水酸基の量 (ミリモル)	524	542	617

[0069] DEG: Diethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH)

Molecular weight = 106, a number of hydroxyl groups = 2-/mol (molecular weight per hydroxyl group; 106/2)

GLY: Glycerol (CH<sub>2</sub>OHCH(OH) CH<sub>2</sub>OH)

Molecular weight: 92, a number of hydroxyl groups = 3-/mol (molecular weight per hydroxyl group; 92/3)

Front Naka, each ink 100ml — to an inner high-boiling point organic solvent Number [ of the amount Y ink DEG of the originating hydroxyl group ] of hydroxyl groups = / (1000x12.0) Number [ of =226 millimol GLY ] of hydroxyl groups = (106/2) / (1000x9.0) (92/3) =293 millimol Y ink 100ml — the number of hydroxyl groups of the amount =of hydroxyl groups226+298=524 millimol M ink DEG originating in an inner high-boiling point organic solvent — number [ of the =(1000x8.0) / (106/2) =151 millimol GLY ] of hydroxyl groups = — / (1000x12.0) (92/3) =391 millimol M ink 100ml — the number of hydroxyl groups of the amount =of hydroxyl groups151+391=542 millimol C ink DEG originating in an inner high-boiling point organic solvent — number [ of the =(1000x6.8) / (106/2) =128 millimol GLY ] of hydroxyl groups = — The amount =of hydroxyl groups128+489=617 millimol ink jet printer originating in an inner high-boiling point organic solvent follows printer driver software. (1000x15.0) / (92/3) =489 millimol Y ink 100ml — For example, \*\*Y, M, supposing it is printable on the following printing conditions C ink — respectively — independent — solid printing: — it is set to 25ml per two 1m of record forms, respectively — as — the ink of printing \*\*2 color — in piles — printing: — it becomes 50% of independent printing conditions — as — the ink of printing \*\*3 color — in piles — printing: — it becomes 35% of independent printing conditions — as — the conditions more than printing — monochrome solid — 2 color solid — it is as follows, when 3 color solid printing is carried out and the amount of hydroxyl groups per two is calculated 1m.

[0070]

(1) Monochrome solid (the amount of the maximum ink = 25 ml/m<sup>2</sup>)

Y: 524x(25/100) =131 millimol M:542x(25/100) =136 millimol C:617x(25/100) =154 millimol (2) 2 color solid (the amount of the maximum ink = 25 ml/m<sup>2</sup>)

Y+M: 0.5x(524+542) x(25/100) =133 millimol M+C:0.5x(542+617) x(25/100) =145 millimol C+Y:0.5x(617+524) x (25/100) =143 millimol (3) 3 color solid (the amount of the maximum ink = 26.25 ml/m<sup>2</sup>)

The amounts of hydroxyl groups which originate in the high-boiling point organic solvent which it is a time of

carrying out monochrome solid printing of the C ink that the amount of the greatest hydroxyl group is breathed out in this printing condition, and is contained in the aqueous recording ink at this time from (1) of the  $0.35 \times (524+542+617) \times (25/100) = 147$  millimol above, (2), and (3) are 154 millimols, and Z is set to 154 millimols / m<sup>2</sup>.

[0071] In this invention, it is desirable that X, Y, and Z fill following condition \*\* and condition \*\*.

[0072] Various kinds of additives can be added in the ink absorption layer of the ink jet record form of condition \*\*  $0.1 \leq X/Y \leq 0.4$  condition \*\*  $Z/Y \leq 3$  this invention.

[0073] Especially, since a cation mordant improves the water resisting property and moisture resistance after printing, it is desirable.

[0074] Although the polymer mordant which has the class [ 1st ] - 3rd class amino group and a quarternary-ammonium-salt radical can be used as a cation mordant, since there being little discoloration by the passage of time and light-fast degradation and the mordanting ability of a color are high enough, the polymer mordant which has a quarternary-ammonium-salt radical is desirable.

[0075] A desirable polymer mordant is the homopolymer of the monomer which has a quarternary-ammonium-salt radical, a copolymer with other monomers, or a condensation polymerization object.

[0076] In the ink absorption layer of the ink jet record form of this invention In addition to a cation mordant, for example, an ultraviolet ray absorbent given in JP,57-74193,A, a 57-87988 official report, and a 62-261476 official report, JP,57-74192,A, a 57-87989 official report, a 60-72785 official report, The fading inhibitor indicated by a 61-146591 official report, JP,1-95091,A, the 3-13376 official report, etc., An anion, a cation or the various surfactants of non-ion, JP,59-42993,A, The fluorescent brightener indicated by a 59-52689 official report, a 62-280069 official report, a 61-242871 official report, JP,4-219266,A, etc., Various well-known additives, such as lubricant, such as a defoaming agent and a diethylene glycol, antiseptics, a thickener, an antistatic agent, and a mat agent, can also be made to contain.

[0077] The ink jet record form kicked to this invention may have the ink absorption layer more than two-layer in the same base material side. When preparing a two or more layers ink absorption layer, that at least one layer should just be an ink absorption layer of this invention, other layers may be swelling layers which made hydrophilic binders, such as gelatin, the subject, or may be ink absorption layers of this invention.

[0078] In the ink jet record form of this invention, in order to prevent that ink imprints in the prevention to which it adheres at the time of piling up immediately after curl prevention and printing to the opposite side of the side which established ink absorptivity, and other ink jet record forms, it is desirable to prepare the back layer of various classes.

[0079] It changes with the class of base material, thickness, and the configurations and thickness of an ink absorption layer, and although it is not fixed, generally a hydrophilic binder and a hydrophobic binder are used for a back layer. Usually, the thickness of a back layer is chosen in 0.1-10 micrometers.

[0080] Moreover, a back layer can adhere as other record forms, and can split-face-ize a front face to prevention, amelioration of note nature, and a pan for amelioration of the conveyance nature within an ink jet recording device. The organic or inorganic particle whose particle size is 2-20 micrometers can be used for split-face-ization.

[0081] In an ink jet record form, the well-known non-absorptivity base material used for the record form for ink jets can be conventionally used suitably as a non-absorptivity base material. As a non-[ these ] absorptivity base material, for example Polyester system resin, diacetate system resin, The bright film which consists of ingredients, such as thoria TESETO system resin, acrylic resin, polycarbonate system resin, polyvinyl chloride system resin, polyimide system resin, cellophane, and celluloid, Or the resin covering paper which prepared the enveloping layer which becomes at least one side of a base paper from the polyolefin resin which added white pigments etc. (the so-called RC paper), Translucent or the opaque base materials which added white pigments, such as the so-called White pet, are used for polyethylene terephthalate.

[0082] It is desirable to perform corona discharge treatment, undercoating processing, etc. in advance of spreading of an ink absorption layer for the purpose, such as to enlarge bond strength of a base material and an ink absorption layer. Furthermore, the ink jet record forms of this invention may not necessarily be being transparent and colorless and the white and colored record sheet.

[0083] Especially since a record image is close to photograph image quality and the image of high quality is moreover obtained by low cost, the ink jet record form using the paper base material which laminated both sides with polyethylene is desirable.

[0084] Hereafter, the paper base material laminated with polyethylene is explained.

[0085] The stencil paper of a paper base material uses wood pulp as the main raw material, if needed, it adds synthetic fibers, such as synthetic pulps, such as polypropylene, or nylon, and polyester, and paper making is carried out. As wood pulp, although both LBKP, LBSP, NBKP, NBSP LDP and NDP LUKP and NUKP can be used, it is desirable to use more many [ for a staple fiber ] LBKP, NBSP(s), LBSP(s), and NDP(s) and LDP(s). However, it reaches LBSP or the ratio of LDP has 10 % of the weight or more and 70 desirable % of the weight or less.



[0086] Chemical pulp with few impurities (for example, sulfate PARUBU, a sulfite bulb) is desirable, and pulp's is [ the pulp which performed bleaching processing and raised the whiteness degree ] useful.

[0087] Hara Kaminaka can add suitably flexible-sized agents, such as moisture hold-back agents, such as paper reinforcing agents, such as white pigments, such as sizing compounds, such as a higher fatty acid and an alkyl ketene dimer, a calcium carbonate, talc, and titanium oxide, starch, polyacrylamide, and polyvinyl alcohol, a fluorescent brightener, and polyethylene glycols, a dispersant, and the 4th class ammonium, etc.

[0088] The freshness of the pulp used for paper making has desirable 200–500 cc by convention of CSF, and 30 thru/or 70% have the desirable sum of weight % of the 24-mesh residue and weight % of the 42-mesh residue as which the fiber length after beating is specified to JIS-P -8207. In addition, as for weight % of the four-mesh residue, it is desirable that it is 20 or less % of the weight.

[0089] The basis weight of stencil paper has 30 thru/or desirable 250g, and 50 thru/or its 200g are especially desirable. The thickness of stencil paper has 40 thru/or desirable 250 micrometers.

[0090] After a paper-making phase or paper making, calender processing of the stencil paper can be carried out, and it can also give the Takahira slippage. A stencil paper consistency has 0.7 thru/or common 1.2 g/m<sup>2</sup> (JIS-P -8118). Furthermore, stencil paper stiffness has 20 thru/or desirable 200g on the conditions specified to JIS-P -8143.

[0091] A surface sizing compound may be applied to a stencil paper front face, and said sizing compound which can carry out the Hara Kaminaka addition, and the same sizing compound can be used as a surface sizing compound.

[0092] When measured by the hot water extraction method specified by JIS-P -8113, as for pH of stencil paper, it is desirable that it is 5–9.

[0093] although the polyethylene which covers a stencil paper front face and a rear face is mainly the polyethylene (LDPE) of a low consistency, and/or polyethylene (HDPE) of high density — other lines — low density polyethylene (LLDPE), polypropylene, etc. can be used.

[0094] As for the polyethylene layer by the side of an ink absorption layer, what added the titanium oxide of a rutile or an anatase mold, and improved opacity and a whiteness degree in polyethylene is desirable as widely performed by the printing paper for photographs. The content of titanium oxide is 4 – 13 % of the weight preferably three to 20% of the weight in general to polyethylene.

[0095] in case melting push appearance also of also using as glossy paper is carried out and it coats polyethylene on a stencil paper front face, polyethylene covering paper can form a mat side and a silky surface which perform the so-called mold attachment processing and are obtained with the usual photographic printing paper, and can also be used.

[0096] After preparing an ink absorption layer and a back layer, the amount of the polyethylene used of the front flesh side of stencil paper is chosen so that there may be no curl, damp and when it is saved by highly humid-ization. Usually, let thickness of the polyethylene layer by the side of 20–40 micrometers and a back layer be the range of 10–30 micrometers for the thickness of the polyethylene layer by the side of an ink absorption layer.

[0097] In this invention, the polyethylene covering paper base material which has the following properties can be used preferably.

[0098] A lengthwise direction by the reinforcement specified by :JIS-P -8113 in hauling strength \*\* 2 thru/or 30kg, a longitudinal direction — 20kg\*\* tear: 1 thru/or on the strength — the convention approach by JIS-P -8116 — a lengthwise direction — 10 — or 200g a longitudinal direction — 20 thru/or 200g\*\* compressibility: — two or more 103 Kgf/cm\*\* surface Beck smoothness: — the conditions specified to JIS-P -8119 when using as glossy paper — 20 seconds or more (if the so-called mold attachment article is suited, you may be less than [ this ].)

\*\* Opacity = by the Measuring condition of straight-line light incidence / diffused-light transparency conditions, various configuration layers, such as an under-coating layer prepared especially the configuration layer of the ink jet record form of 15% or less this invention, i.e., if needed [ an ink absorption layer or if needed ] for an opening mold, suitably 20% or less, can be formed using the approach that the transmission in the beam of light of a visible region is well-known. The desirable formation approach is the approach of applying the coating liquid which constitutes each class on a base material, and drying. The coincidence method of application which can also apply more than two-layer to coincidence, and substitutes spreading of all hydrophilic binder layers for one spreading in this case is desirable.

[0099] As the method of application, the extrusion coat method which uses a hopper the roll coating method, a rod bar coating method, the air-knife-coating method, a spray coating method, the curtain method of application, or given in a U.S. Pat. No. 2681294 specification is used preferably.

[0100] Next, when carrying out ink jet record using the ink jet record form of this invention, the aquosity recording ink to be used is explained.

[0101] Aquosity recording ink usually consists of an additive of others which are added water soluble dye, a solvent, and if needed. Although water soluble dye, such as direct dye used by well-known ink jet record as

water soluble dye, acid dye, basic dye, reactive dye, or a food dye, can be used, direct dye or acid dye is desirable.

[0102] Although the solvent of aqueosity recording ink makes water a subject, when aqueosity recording ink dries, a color deposits, and in order to prevent starting blinding in the supply path of a nozzle tip or aqueosity recording ink, a high-boiling point organic solvent with the boiling point liquefied above 120 degrees C is added at a room temperature. It is required that it should have vapor pressure [ need / therefore / a high-boiling point organic solvent / to have the operation which formed elements, such as a color, deposit when water evaporates, and prevents generating of a big and rough sludge ] far lower than water. Moreover, the miscibility over water needs to be high.

[0103] As a high-boiling point organic solvent used for such the purpose For example, ethylene glycol, propylene glycol, a diethylene glycol, Triethylene glycol, a glycerol, the diethylene-glycol monomethyl ether, The diethylene-glycol monobutyl ether, the triethylene glycol monobutyl ether, The glycerol monomethyl ether, 1 and 2, 3-butane triol, 1 and 2, 4-butane triol, Alcohols, such as 1, 2, 4-pentanetriol, 1 and 2, 6-hexane triol, thiodiglycol, triethanolamine, and a polyethylene glycol (average molecular weight is about 300 or less), are mentioned. Moreover, dimethylformamide, N-methyl pyrrolidone, etc. can be used also besides having described above.

[0104] Also in the high-boiling point organic solvent of these many, the low-grade alkyl ether of polyhydric alcohol, such as polyhydric alcohol, such as a diethylene glycol, triethanolamine, and a glycerol, triethanolamine, and the triethylene glycol monobutyl ether, etc. is desirable.

[0105] As an additive of others which are added by aqueosity recording ink if needed, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rust-proofer, etc. are mentioned, for example.

[0106] Aqueosity recording ink is the purpose which wettability to a record form is made [ purpose ] good, or stabilizes the regurgitation from an ink jet nozzle, and it is desirable in 25 degrees C to have the surface tension of 28 - 40 dyne/cm within the limits preferably 25 to 50 dyne/cm.

[0107] Moreover, in 25 degrees C, 2-10Cp is desirable still more desirable, and the viscosity of aqueosity recording ink is usually 2.5-8Cp. Moreover, when the capacity of the liquid ink drop by which 3-9 are breathed out from a desirable ink nozzle is 1-30pL, since the diameter of a dot with a diameter of about 20-60 micrometers is obtained in the record paper, pH of aqueosity recording ink is desirable. The color-print printed with such a diameter of a dot gives a high-definition image. Furthermore, the capacity of the desirable minimum liquid ink drop is 2-20pL.

[0108] Moreover, when concentration carries out ink jet record about a Magenta and cyanogen at least by the recording method using the aqueosity recording ink which is two kinds different more than twice, since low-concentration ink is used, it is hard coming to carry out discernment of a dot in the highlights section, but this invention can be used also when this recording method is used.

[0109] In the ink jet record approach, various kinds of well-known methods can be conventionally used as the record approach. The detail of the record approach is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

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[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
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EXAMPLE

[Example] This invention is not limited by these examples although an example explains this invention concretely below.

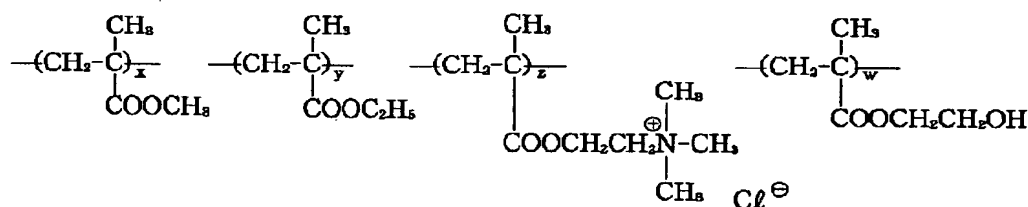
[0111] The paper base material which covered both sides of 1160g of examples/, and the stencil paper for photographs of m2 with polyethylene (the polyethylene layer which contains an anatase mold titanium dioxide with a thickness of 35 micrometers 13% of the weight should be formed in the recording surface side, and as for thickness, a polyethylene layer should be formed in a rear-face side by 25 micrometers, and let  $T_g=65$  degree C acrylic latex resin be solid content on it) The back layer in which 0.6 g/m<sup>2</sup> and a mean diameter make a mat agent the silica which is about 13 micrometers, and contain it two times 0.3 g/m is formed. It prepared.

[0112] Next, in 900ml of pure water, it added, while the mean diameter of a primary particle agitated 180g of particle silica powder which is about 7nm with the high-speed homogenizer, and the silica water dispersion was produced. Next, in this silica water dispersion, 120ml of 20% water solutions of the following cationic mordant was added, the high-speed homogenizer distributed for 30 minutes, and pale clear dispersion liquid were obtained. Next, average degree of polymerization added gradually 400ml (ethyl acetate is contained 4% of the weight) of 5% polyvinyl alcohol water solutions whenever [ saponification / whose ] is 88% by 3500. Subsequently, the amount which shows a borated water solution (20% ethanol content) in Table 1 5% as a hardening agent was added, and further, after adding 50ml of gelatin water solutions 10%, the coating liquid which makes 2100ml to the whole quantity with pure water, and forms an opening layer was produced.

[0113]

[Formula 1]

カチオン性媒染剤



$$x : y : z : w = 25 : 25 : 45 : 5 \text{ (モル比)}$$

$$\text{平均分子量} \approx 23,000$$

[0114] Subsequently, the coating liquid obtained as mentioned above was warmed at 40 degrees C, it applied so that humid thickness might be set to 220 micrometers at the recording surface side of the paper base material covered with the above-mentioned polyethylene, and it was made to cool so that spreading coat temperature may become 15 degrees C or less (for 20 seconds). Subsequently, the 40-degree C wind was sprayed for the 30-degree C wind for 60 seconds for 60 seconds, for 120 seconds and a 35 more-degree C wind were sprayed for 60 seconds and for a 45-degree C wind one by one for 60 seconds, the 25-degree C wind was dried, further, 25 degrees C and the ambient atmosphere of 50% of relative humidity were passed for 120 seconds, gas conditioning was carried out, and the record forms 1-5 were produced.

[0115] In the above-mentioned record forms 1-5, average degree of polymerization produced similarly the record forms 16-20 set to the record forms 11-15 used as 6-10,600ml of record forms which set to 500ml the amount of 5% polyvinyl alcohol water solution whenever [ saponification / whose ] is 88%, and 800ml by 3500.

[0116] The obtained record forms 1-20 were saved for three days at 35 degrees C.

[0117] Next, the aqueous recording ink for ink jets was prepared as follows.

[Yellow ink -1]

Direct yellow 86 2.0g Diethylene glycol 22.2g Glycerol 4.5g 100ml is made with pure water.

[Magenta ink -1]

Direct red 227 1.8g Glycerol 3.5g Diethylene-glycol monobutyl ether 21.5g 100ml is made with pure water.

[Cyanogen INKU 1]

Direct\*blue 199 2.4g Ethylene glycol 16.1g Glycerol 9.5g 100ml is made with pure water.

[0118] The number of hydroxyl groups per 100ml of each above-mentioned aqueous recording ink for ink jets is as follows.

[yellow ink -1] — :566 millimol — /100ml [Magenta INKU 1]:247 millimol / 100ml [cyanogen ink -1]:829 millimol / 100ml, next an ink jet — service water — it printed in the record forms 1-20 using sex recording ink with the on-demand mold ink jet printer (drop capacity =25pL, maximum print density =720dpix720dpi). Printing was performed by monochrome solid, 2 color solid, and 3 color solid printing, respectively.

[0119] When printing, monochrome solid printing was performed with the maximum print density (the amount of ink = 20ml/m<sup>2</sup>), respectively, and, as for 2 color printing, 3 color solid performed each color with 40% of the maximum print density (the amount of ink = 24 ml/m<sup>2</sup>) 60% of the maximum print density (the amount of ink = 24 ml/m<sup>2</sup>).

[0120] The amount of the hydroxyl group originating in the high-boiling point organic solvent in each solid section at this time is as being shown in Table 2 (millimol / m<sup>2</sup>).

[0121]

[Table 2]

単色ベタ			2色ベタ			3色ベタ
Y	M	C	Y+M	M+C	C+Y	Y+M+C
113	49	166	98	129	167	131

[0122] Z (the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form when aqueous recording ink is printed by the maximum delivery in a record form) in the above-mentioned printing conditions of Table 2 to this aqueous recording ink is 167 millimols / m<sup>2</sup>.

[0123] The printed record forms 1-20 were saved for two days at 40 degrees C and 80% of relative humidity. The crack situation of the film surface of the saved sample was visually checked using the magnifier, and the following valuation bases estimated.

a <valuation basis> — O: — although it can check with O:magnifier which the crack has not generated even if it checks with a magnifier, it turns out that the intense crack has occurred in x:viewing understood that the crack has occurred slightly in \*\*:viewing which the crack which cannot be distinguished only visually has generated.

[0124] The obtained result was shown in Table 3.

[0125]

[Table 3]

記録用紙No.	ほう酸		PVAの 水酸基数 (Y)	$\frac{X}{Y}$	$\frac{Z}{Y}$	保存後ひび割れ						
	mg	X				Y	M	C	Y+M	M+C	C+Y	Y+M+C
1 比較例	30	2.5	37.6	0.066	4.44	△	○	×	○	△	×	△
2 比較例	60	5.1	37.6	0.136	4.44	○	◎	×	◎	○	×	○
3 比較例	90	7.8	37.6	0.202	4.44	○	◎	×	◎	○	×	○
4 比較例	150	12.7	37.6	0.338	4.44	○	○	×	○	○	×	○
5 比較例	300	25.3	37.6	0.672	4.44	△	○	×	×	△	×	△
6 本発明	30	2.5	47.0	0.053	3.55	△	○	△	◎	○	△	○
7 本発明	60	5.1	47.0	0.109	3.55	◎	◎	○	◎	◎	○	◎
8 本発明	90	7.8	47.0	0.162	3.55	◎	◎	○	◎	◎	○	◎
9 本発明	150	12.7	47.0	0.270	3.55	◎	◎	○	◎	◎	○	◎
10 比較例	300	25.3	47.0	0.538	3.55	○	◎	×	△	○	×	○
11 比較例	30	2.5	56.4	0.044	2.98	△	○	×	△	○	×	○
12 本発明	60	5.1	56.4	0.091	2.98	○	◎	○	○	○	○	○
13 本発明	90	7.8	56.4	0.136	2.98	◎	◎	◎	◎	◎	◎	◎
14 本発明	150	12.7	56.4	0.226	2.98	◎	◎	◎	◎	◎	◎	◎
15 本発明	300	25.3	56.4	0.452	2.98	◎	◎	○	◎	◎	○	◎
16 比較例	30	2.5	75.2	0.033	2.23	△	○	×	○	○	×	○
17 本発明	60	5.1	75.2	0.068	2.23	◎	◎	○	◎	◎	○	◎
18 本発明	90	7.8	75.2	0.101	2.23	◎	◎	◎	◎	◎	◎	◎
19 本発明	150	12.7	75.2	0.169	2.23	◎	◎	◎	◎	◎	◎	◎
20 本発明	300	25.3	75.2	0.337	2.23	◎	◎	◎	◎	◎	◎	◎

[0126] The result of Table 3 shows that a crack does not arise in the solid printing section even if saved under an elevated temperature and highly humid when satisfying both condition \*\*s and condition \*\*s of this invention.

[0127] Especially, when X/Y is 0.4 or less [ 0.1 or more ] and Z/Y is three or less, it turns out that there are few cracks.

[0128] The aqueosity recording ink for example 2 ink jets was prepared as follows.

[Yellow INKU 2]

Direct yellow 86 2.0g diethylene glycol 21.5g glycerol 100ml is made with 9.8g pure water.

[Magenta ink -2]

Direct red 227 1.8g glycerol 10.5g diethylene glycol 100ml is made with 19.5g pure water.

[Cyanogen ink -2]

Direct blue 199 2.4g ethylene glycol 16.1g glycerol 100ml is made with 12.9g pure water.

[0129] The number of hydroxyl groups per 100ml of each above-mentioned aqueosity recording ink for ink jets is as follows.

[yellow ink -1] — :725 millimol / 100ml [Magenta ink -1] — the on-demand mold ink jet printer used in :710 millimol / 100ml [cyanogen ink -1]:940 millimol / the 100ml example 1 — using — printing conditions given in an example 1 — monochrome solid and 2 color solid — 3 color solid printing was carried out.

[0130] The amount of the hydroxyl group originating in the high-boiling point organic solvent in each solid section at this time is as being shown in Table 4 (millimol / m2).

[0131]

[Table 4]

単色ベタ			2色ベタ			3色ベタ
Y	M	C	Y+M	M+C	C+Y	Y+M+C
145	142	188	172	198	200	190

[0132] Z (the maximum amount of hydroxyl groups of the amounts of hydroxyl groups in the high-boiling point organic solvent contained in per unit area of the printed record form when aqueosity recording ink is printed by the maximum delivery in a record form) in the above-mentioned printing conditions of Table 4 to this aqueosity recording ink is 200 millimols / m2.

[0133] Subsequently, the crack situation of a film surface as well as an example 1 was evaluated about the record forms 1-20 obtained by printing.

[0134] The obtained result is shown in Table 5.

[0135]

[Table 5]

記録用紙No.		ほう酸		PVAの 水酸基数 (Y)	$\frac{X}{Y}$	$\frac{Z}{Y}$	保存後ひび割れ						
		mg	X				Y	M	C	Y+M	M+C	C+Y	Y+M+C
1	比較例	30	2.5	37.6	0.066	5.32	×	×	×	×	×	×	×
2	比較例	60	5.1	37.6	0.136	5.32	△	△	×	×	×	×	×
3	比較例	90	7.6	37.6	0.202	5.32	△	△	×	×	×	×	×
4	比較例	150	12.7	37.6	0.338	5.32	○	○	×	×	×	×	×
5	比較例	300	25.3	37.6	0.672	5.32	△	△	×	×	×	×	×
6	比較例	30	2.5	47.0	0.053	4.25	×	×	×	×	×	×	×
7	比較例	60	5.1	47.0	0.109	4.25	○	○	×	×	×	×	×
8	比較例	90	7.6	47.0	0.162	4.25	○	○	△	△	×	×	×
9	比較例	150	12.7	47.0	0.270	4.25	○	○	△	△	×	×	×
10	比較例	300	25.3	47.0	0.538	4.25	△	△	×	×	×	×	×
11	比較例	30	2.5	56.4	0.044	3.55	×	×	×	×	×	×	×
12	本発明	60	5.1	56.4	0.091	3.55	○	○	○	○	○	○	○
13	本発明	90	7.6	56.4	0.136	3.55	◎	◎	○	○	○	○	○
14	本発明	150	12.7	56.4	0.226	3.55	◎	◎	○	○	○	○	○
15	本発明	300	25.3	56.4	0.452	3.55	○	○	○	○	○	○	○
16	比較例	30	2.5	75.2	0.033	2.67	×	×	×	×	×	×	×
17	本発明	60	5.1	75.2	0.068	2.67	◎	◎	○	○	○	○	○
18	本発明	90	7.6	75.2	0.101	2.67	◎	◎	◎	◎	◎	◎	◎
19	本発明	150	12.7	75.2	0.169	2.67	◎	◎	◎	◎	◎	◎	◎
20	本発明	300	25.3	75.2	0.337	2.67	◎	◎	◎	◎	◎	◎	◎

[0136] When satisfying both condition \*\*s and condition \*\*s of this invention like an example 1 from the result of Table 5, it turns out whether even if it saves all under an elevated temperature and highly humid, the crack has hardly arisen, and that it is not generated at all.

[Translation done.]

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(54)【発明の名称】 インクジェット記録方法

(57)【要約】 (修正有)

【課題】 記録用紙に、水性記録液で記録した用紙を高  
温高湿下で保存しても、ひび割れを生じないインクジェ  
ット記録方法を提供する。

【解決手段】 非吸水性支持体上のインク吸収層中に、  
ポリビニルアルコール、無機微粒子及びほう酸またはそ  
の塩を含有する記録用紙に、水酸基を有する化合物を高  
沸点有機溶媒として含有する水性記録液で記録する記録  
方法において、下記の条件①及び条件②を同時に満足す  
る量にしたインクジェット記録方法。

条件①  $0.05 \leq X/Y \leq 0.5$

条件②  $Z/Y \leq 4$

式中、Xは、記録用紙のインク吸収層中に含まれるほう  
酸またはその塩の量 (ミリモル/ $m^2$ )、Yは、記録用紙  
のインク吸収層中に含まれるポリビニルアルコール中の  
水酸基の量 (ミリモル/ $m^2$ )、Zは、水性記録液を記録  
用紙に最大吐出量で印字したとき、印字された記録用紙  
の単位面積当たりに含まれる高沸点有機溶媒中の最大の  
水酸基量 (ミリモル/ $m^2$ )

## 【特許請求の範囲】

【請求項 1】 非吸水性支持体上のインク吸収層中に、ポリビニルアルコール、無機微粒子及びほう酸またはその塩を含有するインクジェット記録用紙に、インクジェット記録装置を用い、水酸基を有する化合物を高沸点有機溶媒として含有する水性記録液で記録するインクジェット記録方法において、記録用紙のインク吸収層中に含まれる単位面積当たりのほう酸またはその塩の量、記録用紙のインク吸収層中に含まれるポリビニルアルコール中の単位面積当たりの水酸基の量、水性記録液を記録用紙に最大吐出量で印字したとき、印字された記録用紙の単位面積当たりに含まれる高沸点有機溶媒中の水酸基量のうちの最大の水酸基量を下記の条件①及び条件②を同時に満足する量にしたことを特徴とするインクジェット記録方法。

条件①  $0.05 \leq X/Y \leq 0.5$

条件②  $Z/Y \leq 4$

式中、

Xは、記録用紙のインク吸収層中に含まれる単位面積当たりのほう酸またはその塩の量（ミリモル/ $\text{m}^2$ ）

Yは、記録用紙のインク吸収層中に含まれるポリビニルアルコール中の単位面積当たりの水酸基の量（ミリモル/ $\text{m}^2$ ）

Zは、水性記録液を記録用紙に最大吐出量で印字したとき、印字された記録用紙の単位面積当たりに含まれる高沸点有機溶媒中の水酸基量のうちの最大の水酸基量（ミリモル/ $\text{m}^2$ ）

を表す。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、インクジェット記録用紙に水性インクを用いて記録を行うインクジェット記録方法に関し、更に詳しくは、印字後の皮膜の劣化を防止した、高いインク吸収性を有する空隙型のインク吸収層を有するインクジェット記録用紙を用いて行うインクジェット記録方法に関する。

## 【0002】

【従来の技術】インクジェット記録は、インクの微小液滴を種々の作動原理により飛翔させて紙などの記録シートに付着させ、画像・文字などの記録を行うものであるが、比較的高速、低騒音、多色化が容易である等の利点を有している。この方式で従来から問題となっていたノズルの目詰まりとメンテナンスについては、インク及び装置の両面から改良が進み、現在では各種プリンター、ファクシミリ、コンピューター端末等のさまざまな分野で急速に普及している。

【0003】その詳細は、例えば、インクジェット記録技術の動向（中村孝一編、平成7年3月31日、日本科学情報株式会社発行）に記載されている。

【0004】インクジェット記録用紙としては、従来か

ら種々の記録用紙が用いられている。例えば、普通紙、親水性バインダーと無機顔料から成る層を塗設した各種の塗工紙（アート紙、コート紙、キャストコート紙等）、更には、両面をプラスチック樹脂で被覆した各種の紙、透明または不透明の各種のプラスチックフィルムよりなる支持体上に記録層としてインク吸収層を塗設したインクジェット記録用紙が用いられている。

【0005】上記インク吸収層は、親水性バインダーを主体に構成された膨潤型のインク吸収層、記録層中に空隙を設けた空隙型のインク吸収層に大きく分けられる。

【0006】空隙型のインク吸収層は、層に形成された空隙にインクを保持するものであり、空隙は、各種の無機固体微粒子や有機の固体微粒子を皮膜中に含有させることによって形成している。

【0007】インクジェット記録用紙としては、印字ドットの濃度が高く、色調が明るく鮮やかであること、インクの吸収が早く、印字ドットが重なった場合においてもインクが流れ出したり滲んだりしないこと、印字ドットの横方向への拡散が必要以上に大きくなく、かつ、周辺が滑らかでばやけないこと等の性能が要求される。

【0008】インク吸収層のインク吸収速度が遅い場合には、2色以上のインク液滴が重なって記録される際に、記録用紙上でインクの液滴がハジキ現象を起こしてムラを生じたり、また、異なる色の境界領域でお互いの色が惨んだりして画質を大きく低下させるので、インクジェット記録用紙には、高いインク吸収性を持たせることが要求されている。

【0009】これらの問題を解決するために、例えば、特開昭52-53012号公報に記載されている低サイズ原紙に表面加工用の塗料を湿潤させた記録用紙、特開昭55-5830号公報に記載されている支持体表面にインク吸収性の塗層を設けた記録用紙、特開昭56-157号公報に記載されている被覆層中の顔料として非膠質シリカ粉末を含有する記録用紙、特開昭57-107878号公報に記載されている無機顔料と有機顔料を併用した記録用紙、特開昭58-110287号公報に記載されている2つの空孔分布ピークを有する記録用紙、特開昭62-111782号公報に記載されている上下2層の多孔質層からなる記録用紙、特開昭59-68292号公報、同59-123696号公報及び同60-18383号公報などに記載されている不定形亀裂を有する記録用紙、特開昭61-135786号公報、同61-148092号公報及び同62-149475号公報等に記載されている微粉末層を有する記録用紙、特開昭63-252779号公報、特開平1-108083号公報、同2-136279号公報、同3-65376号公報及び同3-27976号公報等に記載されている特定の物性値を有する顔料や微粒子シリカを含有する記録用紙、特開昭57-14091号公報、同60-219083号公報、同60-210984号公報、同61-20797号公報、同61-188183号公報、特開平5-278324号公報、同6-92011号公報、同6-183134号公報、同7-137431号公報及び同7-276789号公報等に記載されているコロイド状シリ



カ等の微粒子シリカを含有する記録用紙、及び特開平2-276671号公報、同3-67684号公報、同3-215082号公報、同3-251488号公報、同4-67986号公報、同4-263983号公報及び同5-16517号公報などに記載されているアルミナ水和物微粒子を含有する記録用紙等、非常に多くの技術が提案されている。

【0010】インクジェット記録用紙において、支持体自身に吸水性がある場合には、高い吸収容量とインク吸収性を持っておりインクの吸収という観点からすれば好ましいが、インクジェット記録後に、支持体が波打ち、画像上にシワが生じたり、染料が支持体中に部分的に浸透して濃度が出にくいという問題がある。

【0011】支持体为非吸水性であるときには上記の欠点は発生せず、濃度が高い鮮明な画像が得られるが、インク吸収層中に形成されるインクを吸収する空隙の量が制限を受けるという問題があった。

【0012】例えば、乾燥膜厚が $40\mu\text{m}$ であるインク吸収層において、固形分が厚さ $22\mu\text{m}$ の皮膜を形成することができる量あったとすると、空隙量はインクジェット記録用紙 $1\text{m}^2$ 当たり $18\text{ml}/\text{m}^2$ しかないことになり、記録方式にもよるが、最大インク量付近でインクを吸収する空隙の容量が不足する場合が生じ得る。

【0013】塗布膜厚を増大させれば高い空隙容量が得られるが、塗布膜厚を増大させると、皮膜が脆弱になり、低湿度の下でヒビ割れが生じたり、支持体に対する接着性が低下するという問題が生じる。

【0014】本出願人は、上記の問題点を解決するために、空隙構造を形成する親水性バインダーと架橋し得る硬膜剤を添加することにより皮膜の造膜性や脆弱性を改良する方法を提案した。(特願平8-283636号)

親水性バインダーとしてポリビニルアルコールを、硬膜剤としてほう酸またはその塩を用いて空隙型のインク吸収層を形成した空隙型のインクジェット記録用紙は、インクジェット記録用紙として特に好ましいものである。

【0015】しかしながら、水酸基を有する化合物を高沸点有機溶媒として含有する水性インクで、上記の親水性バインダーとしてポリビニルアルコールを、硬膜剤としてほう酸またはその塩を用いたインク吸収層を有するインクジェット記録用紙にインクジェット記録をしたとき、記録した用紙を高温・高湿下で保存しておくと、部分的に、皮膜にひび割れが生じてしまう問題が生じることが判明した。

【0016】この原因について種々検討したところ、水性記録液中に含まれる水酸基を含む化合物の作用により皮膜が劣化するためであることが判明した。

【0017】また、このひび割れは、空隙を形成するために用いている無機微粒子の含有量がポリビニルアルコールに対して重量比で2未満である場合には殆ど発生しないことからすると、空隙を形成するために多量に用いる無機微粒子が、印字部でのポリビニルアルコールの造

膜性を低下させるためであると推定される。

#### 【0018】

【本発明が解決しようとする課題】本発明は上記の実態に鑑みてなされたものであって、本発明の目的は、水酸基を有する化合物を高沸点有機溶媒として含有する水性記録液で、上記の親水性バインダーとしてポリビニルアルコールを、硬膜剤としてほう酸またはその塩を用いたインク吸収層を有するインクジェット記録用紙にインクジェット記録をしたとき、記録した用紙を高温高湿下で保存しても、ひび割れを生じないインクジェット記録方法を提供することにある。

#### 【0019】

【課題を解決するための手段】上記課題は、非吸水性支持体上のインク吸収層中に、ポリビニルアルコール、無機微粒子及びほう酸またはその塩を含有するインクジェット記録用紙に、インクジェット記録装置を用い、水酸基を有する化合物を高沸点有機溶媒として含有する水性記録液で記録するインクジェット記録方法において、記録用紙のインク吸収層中に含まれる単位面積当たりのほう酸またはその塩の量、記録用紙のインク吸収層中に含まれるポリビニルアルコール中の単位面積当たりの水酸基の量、水性記録液を記録用紙に最大吐出量で印字したとき、印字された記録用紙の単位面積当たりに含まれる高沸点有機溶媒中の水酸基量のうちの最大の水酸基量を下記の条件①及び条件②を同時に満足する量にしたことを特徴とするインクジェット記録方法。

【0020】条件①  $0.05 \leq X/Y \leq 0.5$

条件②  $Z/Y \leq 4$

式中、Xは、記録用紙のインク吸収層中に含まれる単位面積当たりのほう酸またはその塩の量(ミリモル/ $\text{m}^2$ )

Yは、記録用紙のインク吸収層中に含まれるポリビニルアルコール中の単位面積当たりの水酸基の量(ミリモル/ $\text{m}^2$ )

Zは、水性記録液を記録用紙に最大吐出量で印字したとき、印字された記録用紙の単位面積当たりに含まれる高沸点有機溶媒中の水酸基量のうちの最大の水酸基量(ミリモル/ $\text{m}^2$ )を表す。

【0021】以下本発明を詳細に説明する。

【0022】本発明に用いられるインクジェット記録用紙は非吸水性支持体上に空隙型のインク吸収層(以下、空隙層ということもある。)を有するものである。

【0023】本発明では、空隙層に高い空隙率が得られることから、ポリビニルアルコールが親水性バインダーとして用いられている。ポリビニルアルコールは無機微粒子と相互作用をして軟凝集を形成しやすいために効率的に空隙を形成することができる。

【0024】本発明でいうポリビニルアルコールには、カチオン変性ポリビニルアルコール、ノニオン変性ポリビニルアルコール及びアニオン変性ポリビニルアルコー

ルも含まれる。

【0025】ポリビニルアルコールの平均重合度は、造膜性を改良する観点からすると、1000～5000のが好ましく、2000以上が特に好ましい。

【0026】ポリビニルアルコールのケン化度は70～100%のものが好ましく、80～100%のものが特に好ましい。

【0027】カチオン変性ポリビニルアルコールとは、例えば、特開昭61-10483号公報に記載されているような、第1～3級アミノ基や第4級アンモニウム基をポリビニルアルコールの主鎖または側鎖中に有するポリビニルアルコールのことであり、カチオン性基を有するエチレン性不飽和単量体と酢酸ビニルとの共重合体をケン化することにより得られる。

【0028】カチオン性基を有するエチレン性不飽和単量体としては、例えば、トリメチルー（2-アクリルアミド-2，2-ジメチルエチル）アンモニウムクロライド、トリメチルー（3-アクリルアミド-3，3-ジメチルプロピル）アンモニウムクロライド、N-ビニルイミダゾール、N-ビニルー2-メチルイミダゾール、N-（3-ジメチルアミノプロピル）メタクリルアミド、ヒドロキシエチルトリメチルアンモニウムクロライド、トリメチルー（メタクリルアミドプロピル）アンモニウムクロライド、N-（1，1-ジメチルー3-ジメチルアミノプロピル）アクリルアミド等が挙げられる。

【0029】カチオン性基を有するエチレン性不飽和単量体と酢酸ビニルとの共重合体において、カチオン変性基含有単量体の比率は、酢酸ビニルに対して0.1～10モル%、好ましくは0.2～5モル%である。

【0030】アニオン変性ポリビニルアルコールとしては、例えば、特開平1-206088号公報に記載されているようなアニオン性基を有するポリビニルアルコール、特開昭61-237681号公報及び同63-307979号公報に記載されているようなビニルアルコールと水溶性基を有するビニル化合物との共重合体、特開平7-285265号公報に記載されているような水溶性基を有する変性ポリビニルアルコールが挙げられる。

【0031】ノニオン変性ポリビニルアルコールとしては、例えば、特開平7-9758号公報に記載されているようなポリアルキレンオキサイド基をビニルアルコールの一部に付加したポリビニルアルコール誘導体、特開平8-25795号公報に記載された疎水性基を有するビニル化合物とビニルアルコールとのブロック共重合体が挙げられる。

【0032】空隙層中には、ポリビニルアルコールとともに、他の親水性バインダーを含有させることができる。他の親水性バインダーはポリビニルアルコールに対して概ね20重量%以下であることが好ましい。

【0033】本発明において、無機微粒子はインク吸収層に空隙を形成するために用いられている。

【0034】無機微粒子としては、例えば、軽質炭酸カルシウム、重質炭酸カルシウム、炭酸マグネシウム、カオリン、クレー、タルク、硫酸カルシウム、硫酸バリウム、二酸化チタン、酸化亜鉛、水酸化亜鉛、硫化亜鉛、炭酸亜鉛、ハイドロタルサイト、珪酸アルミニウム、ケイソウ土、珪酸カルシウム、珪酸マグネシウム、合成非晶質シリカ、コロイダルシリカ、アルミナ、コロイダルアルミナ、擬ペーマイト、水酸化アルミニウム、リトポン、ゼオライト、水酸化マグネシウム等の白色無機顔料等を挙げることができる。

【0035】無機微粒子は、バインダー中に1次粒子のまま均一に分散されていてもよく、2次凝集粒子を形成してバインダー中に均一に分散されていてもよい。

【0036】無機微粒子は、1次粒子の粒径が30nm以下のものを使用することが光沢性の観点から好ましい。

【0037】1次粒子の平均粒径が30nmを超える無機微粒子を使用した場合、媒染剤としてカチオン型の水溶性ポリマー媒染剤を用いた場合、カチオン型の水溶性ポリマー媒染剤と凝集が起こりやすくなり、形成した凝集粒子もより粗大化して光沢性が低下してしまう。特に好ましい1次粒子の粒径は20nm以下である。

【0038】1次粒子の粒径の下限は特に限定されないが、粒子の製造上の観点から概ね3nm以上、特に6nm以上である。

【0039】無機微粒子の平均粒径は、粒子そのものあるいは空隙層の断面や表面に現れた粒子を電子顕微鏡で観察し、100個の任意の粒子の粒径を求めてその単純平均値（個数平均）として求められる。ここで個々の粒子の粒径はその投影面積に等しい円を仮定したときの直径で表したものである。

【0040】無機微粒子としては、1次粒子の平均粒径が50nm以下の無機微粒子と平均粒径が50nm以上の無機微粒子を併用することも可能であるが、この場合、50nmを超える無機微粒子の比率は全無機微粒子に対して50重量%以下とするのが好ましく、20重量%以下がより好ましい。

【0041】濃度の高い画像が形成される、鮮明な画像が記録できる、低コストで製造できる等の点からすると、無機微粒子としては、気相法により合成された微粒子シリカ及びコロイダルシリカから選ばれた無機微粒子を用いることが好ましく、気相法により合成されたシリカを用いることが最も好ましい。

【0042】気相法により合成された微粒子シリカは、通常、四塩化珪素を水素及び酸素と共に高温で燃焼して得ることができ、1次粒子の粒子径が5～500nmのシリカ粉末である。特に30nm以下の1次粒子径を有するものが光沢性の点で好ましい。

【0043】現在、このような気相法により合成された微粒子シリカは市販されており、市販の微粒子シリカには、日本アエロジル社の各種のアエロジルがある。

【0044】本発明で好ましく用いられるコロイダルシリカは、珪酸ナトリウムを酸等によって複分解したり、イオン交換樹脂層を通過させたりして得られるシリカゲルを加熱熟成して得られるものである。このコロイダルシリカをインクジェット記録用紙に使用することは、例えば、特開昭57-14091号公報、同60-219083号公報、同60-219084号公報、同61-20792号公報、同61-188183号公報、同63-17807号公報、特開平4-93284号公報、同5-278324号公報、同6-92011号公報、同6-183134号公報、同6-297830号公報、同7-81214号公報、同7-101142号公報、同7-179029号公報、同7-137431号公報、及び国際特許公開WO94/26530号公報などに記載されている。

【0045】コロイダルシリカの好ましい粒子径は、通常、5～100nmであるが、粒子径7～50nmのものが更に好ましい。

【0046】気相法により合成された微粒子シリカやコロイダルシリカは、その表面をカチオン変成してもよく、例えば、Al、Ca、Mg及びBa等の無機塩で処理してもよい。

【0047】無機微粒子は、ポリビニルアルコールに対して重量比率で2～10の範囲で用いることが好ましく、特に3～9が好ましい。

【0048】ほう酸またはその塩は、硬膜剤として用いられている。

【0049】ほう酸またはその塩（以下、硬膜剤ということもある。）とは、硼素原子を中心原子とする酸素酸及びその塩のことであり、具体的には、オルトほう酸、メタほう酸、次ほう酸、四ほう酸、五ほう酸及びそれらの塩が挙げられる。

【0050】硬膜剤は、空隙層を形成する塗布液中に添加してもよく、空隙層に隣接するその他の層を形成する塗布液中に添加してもよい。また、予め硬膜剤を含有する塗布液を塗布してある支持体上に硬膜剤を含有していない空隙層を形成する塗布液を塗布したり、さらには、硬膜剤を含有していない空隙層を形成する塗布液を塗布乾燥した後に硬膜剤溶液をオーバーコートするなどして空隙層に硬膜剤を供給することができる。製造が容易である点からすると、空隙層を形成する塗布液またはこれに隣接する層の塗布液中に硬膜剤を添加して、空隙層を形成するのが好ましい。

【0051】次に、本発明を規定する下記の条件①と条件②について説明する。

【0052】条件①  $0.05 \leq X/Y \leq 0.5$

条件②  $Z/Y \leq 4$

Xは、記録用紙のインク吸収層中に含まれる単位面積当たりのほう酸またはその塩の量（ミリモル/ $m^2$ ）

Yは、記録用紙のインク吸収層中に含まれるポリビニルアルコール中の単位面積当たりの水酸基の量（ミリモル/ $m^2$ ）

Zは、水性記録液を記録用紙に最大吐出量で印字したと

き、印字された記録用紙の単位面積当たりに含まれる高沸点有機溶媒中の水酸基量のうちの最大の水酸基量（ミリモル/ $m^2$ ）

本発明の効果を得るためには、記録用紙のインク吸収層中に含まれる単位面積当たりのほう酸またはその塩の量（ミリモル/ $m^2$ ）、記録用紙のインク吸収層中に含まれるポリビニルアルコール中の単位面積当たりの水酸基の量（ミリモル/ $m^2$ ）及び水性記録液を記録用紙に最大吐出量で印字したとき、印字された記録用紙の単位面積当たりに含まれる高沸点有機溶媒中の水酸基量のうちの最大の水酸基量（ミリモル/ $m^2$ ）の3つのパラメーターが上記条件①と条件②を同時に満足することが必要である。

【0053】本発明では、上記①と②の条件が同時に満足されてはじめて高湿度の条件で保存した場合の皮膜劣化が防止できる。

【0054】条件①は、ポリビニルアルコールの水酸基量とほう酸またはその塩の量との比率が、特定の範囲にあることが必要であることを示し、条件②は、ポリビニルアルコールの水酸基量と水性記録液を記録用紙に最大吐出量で印字したとき、印字された記録用紙の単位面積当たりに含まれる高沸点有機溶媒中の水酸基量のうちの最大の水酸基量との比率が、特定の範囲にあることが必要であることを示している。

【0055】上記の条件①と条件②を同時に満足されなければならない理由ははっきりしないが、皮膜として十分な強度を持たせるためには、ポリビニルアルコール中の水酸基の量に対して硬膜剤の量が適度の比率を持つて存在することが必要であり、また、水性記録液が含有する高沸点有機溶媒の水酸基がポリビニルアルコールの水酸基と競争的に硬膜剤と反応するので、硬膜剤とポリビニルアルコールの反応を維持するために、ポリビニルアルコールの水酸基に対して水性記録液が含有する高沸点有機溶媒の水酸基量の比率が重要性を有するのではないかと推定される。

【0056】次、にX、Y、Zについて更に詳細に説明する。

【0057】Xは、記録用紙のインク吸収層中に含まれる単位面積当たりのほう酸またはその塩の量をミリモル/ $m^2$ で表したものである。

【0058】Xは、ほう酸またはその塩のグラム分子をほう酸またはその塩に含まれるほう素原子の数で割った値を1モルとして計算したものである。

【0059】例えば、オルトホウ酸（ $H_3BO_3$ ）またはその塩、メタほう酸（ $HBO_2$ ）またはその塩が記録用紙1 $m^2$ 当たりに換算して0.01モル含有している場合には、Xは0.01（モル/ $m^2$ ）、即ち、10（ミリモル/ $m^2$ ）である。また、1分子中にほう素原子を4つ有する四ほう酸塩（例えば、 $Na_2B_4O_7$ 等）が記録用紙1 $m^2$ 当たりに換算して0.01モル含有している場合には、Xは4×

0.01 (モル/㎡)、即ち、40 (ミリモル/㎡) である。  
また、1分子中にほう素原子を5つ有する五ほう酸塩  
(例えば、 $\text{NaB}_5\text{O}_8$ 等) を記録用紙1㎡当りに換算  
して0.01モル含有している場合には、Xは $5 \times 0.01$  (モ  
ル/㎡)、即ち、50 (ミリモル/㎡) である。

【0060】ほう酸またはその塩を複数併用した場合には、それぞれについてXを求め、それらを合計したもので表される。

【0061】Yは、ケン化度p (%) のポリビニルアルコールの見かけの分子量 ( $=86-0.42 \times p$ ) (酢酸ビニルの分子量; 86、ビニルアルコールの分子量; 44) を用い、記録用紙1㎡当りに換算したポリビニルアルコールの量がy gであるときには、 $Y = (1000 \times y) \times (p / 100) / (86 - 0.42 \times p) = 10 \times p \times y / (86 - 0.42 \times p)$  (ミリモル/㎡) で表される。

【0062】例えば、ケン化度が88%のポリビニルアルコールを記録用紙1㎡当り3 g用いたとき、 $Y = 10 \times 88 \times 3 / (86 - 0.42 \times 88) = 53.8$  (ミリモル/㎡) になる。

【0063】Zは、水性記録液を記録用紙に最大吐出量で印字したとき、印字された記録用紙の単位面積当りに含まれる高沸点有機溶媒中の水酸基量のうちの最大の水酸基量をミリモル/㎡で表したものである。

【0064】水性記録液を記録用紙に最大吐出量で印字したとき、印字された記録用紙の単位面積当りに含まれる高沸点有機溶媒中の水酸基量とは、プリンタードラ

イバースフトによって制御されたインクジェット記録装置で最大吐出量でベタ印字されたときに、記録用紙の単位面積当りに含まれる水性記録液中の高沸点有機溶媒に由来する水酸基の量をいう。

【0065】ここで高沸点有機溶媒とは、沸点が120℃以上の有機溶媒をいい、これに満たない沸点を有する有機溶媒は含まれない。

【0066】一般に、カラーインクジェット記録においては、水性記録液として、イエロー、マゼンタ、シアン及び必要に応じてブラックの各インクが併用されており、場合によってはそれぞれに染料濃度が異なる複数のインクを用いることもある。このような場合、インクジェット記録装置で、プリンタードライバースフトに従った種々のインクの組み合わせの最大吐出量でベタ印字したときに、それぞれの組み合わせにおいて、記録用紙の単位面積当りに含まれる水性記録液中の高沸点有機溶媒に由来する水酸基の量が求められるが、水性記録液を記録用紙に最大吐出量で印字したとき、印字された記録用紙の単位面積当りに含まれる高沸点有機溶媒中の水酸基量のうちの最大の水酸基量とは、これら求められた水酸基の量のうちの最大のものをいう。

【0067】以下に、水性記録液として以下の組成を有する3種類のインクを使用した場合について、Zを求める方法を具体的に説明する。

【0068】

【表1】

	Yインク	Mインク	Cインク
染料	2.1g	1.7g	1.9g
DEG	12.0g	8.0g	6.8g
GLY	9.0g	12.0g	15.0g
純水で仕上げ	100ml	100ml	100ml
各100ml中の水酸基の量 (ミリモル)	524	542	617

【0069】DEG: ジエチレングリコール ( $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ )

分子量=106、水酸基数=2/モル (水酸基1つ当たりの分子量; 106/2)

GLY: グリセリン ( $\text{CH}_2\text{OHCH}(\text{OH})\text{CH}_2\text{OH}$ )

分子量: 92、水酸基数=3/モル (水酸基1つ当たりの分子量; 92/3)

表中、各インク100ml中の高沸点有機溶媒に由来する水酸基の量

Yインク

DEGの水酸基数 =  $(1000 \times 12.0) \div (106 / 2) = 226$  ミリモル

GLYの水酸基数 =  $(1000 \times 9.0) \div (92 / 3) = 293$  ミリモル

Yインク100ml中の高沸点有機溶媒に由来する水酸基量 =  $226 + 298 = 524$  ミリモル

Mインク

DEGの水酸基数 =  $(1000 \times 8.0) \div (106 / 2) = 151$  ミリモル

GLYの水酸基数 =  $(1000 \times 12.0) \div (92 / 3) = 391$  ミリモル

Mインク100ml中の高沸点有機溶媒に由来する水酸基量 =  $151 + 391 = 542$  ミリモル

Cインク

DEGの水酸基数 =  $(1000 \times 6.8) \div (106 / 2) = 128$  ミリモル

GLYの水酸基数 =  $(1000 \times 15.0) \div (92 / 3) = 489$  ミリモル

Yインク100ml中の高沸点有機溶媒に由来する水酸基量

$=128+489=617$ ミリモル

インクジェットプリンターがプリンタードライバーソフトに従って、例えば、下記の印字条件で印字できるものであるとすると、

① Y、M、Cインクをそれぞれ単独でベタ印字：それぞれ、記録用紙  $1\text{m}^2$  当たり  $25\text{ml}$  になるように印字

② 2色のインクを重ねて印字：単独の印字条件の50%になるように印字

③ 3色のインクを重ねて印字：単独の印字条件の35%になるように印字

以上の条件で単色ベタ、2色ベタ、3色ベタ印字したときの  $1\text{m}^2$  当たりの水酸基量を求めると以下になる。

#### 【0070】

(1) 単色ベタ (最大インク量  $=25\text{ml}/\text{m}^2$ )

Y:  $524 \times (25/100) = 131$ ミリモル

M:  $542 \times (25/100) = 136$ ミリモル

C:  $617 \times (25/100) = 154$ ミリモル

(2) 2色ベタ (最大インク量  $=25\text{ml}/\text{m}^2$ )

Y+M:  $0.5 \times (524+542) \times (25/100) = 133$ ミリモル

M+C:  $0.5 \times (542+617) \times (25/100) = 145$ ミリモル

C+Y:  $0.5 \times (617+524) \times (25/100) = 143$ ミリモル

(3) 3色ベタ (最大インク量  $=26.25\text{ml}/\text{m}^2$ )

$0.35 \times (524+542+617) \times (25/100) = 147$ ミリモル

上記の(1)、(2)、(3)から、この印字条件において、最大の水酸基の量が吐出されるのはCインクを単色ベタ印字したときであり、このときの水性記録液中に含まれる高沸点有機溶媒に由来する水酸基量は  $154$ ミリモルであり、Zは  $154$ ミリモル/ $\text{m}^2$ となる。

【0071】本発明においては、X、Y、Zが下記の条件③及び条件④を満たすことが好ましい。

【0072】条件③  $0.1 \leq X/Y \leq 0.4$

条件④  $Z/Y \leq 3$

本発明のインクジェット記録用紙のインク吸収層には、各種の添加剤を添加することができる。

【0073】中でもカチオン媒染剤は、印字後の耐水性や耐湿性を改良するので好ましい。

【0074】カチオン媒染剤としては、第1級～第3級アミノ基及び第4級アンモニウム塩基を有するポリマー媒染剤を用いることができるが、経時での変色や耐光性の劣化が少ないこと、染料の媒染能が充分高いことなどから、第4級アンモニウム塩基を有するポリマー媒染剤が好ましい。

【0075】好ましいポリマー媒染剤は、第4級アンモニウム塩基を有するモノマーの単独重合体やその他のモノマーとの共重合体または縮重合体である。

【0076】本発明のインクジェット記録用紙のインク吸収層には、カチオン媒染剤以外に、例えば、特開昭57-74193号公報、同57-87988号公報及び同62-261476号公報に記載の紫外線吸収剤、特開昭57-74192号公報、同57-87989号公報、同60-72785号公報、同61-146591号公報、特開平1-95091号公報及び同3-13376号公報等に記載されている退色防止剤、アニオン、カチオンまたは非イオンの各種界面活性剤、特開昭59-42993号公報、同59-52689号公報、同62-280069号公報、同61-242871号公報及び特開平4-219266号公報等に記載されている蛍光増白剤、消泡剤、ジェチレングリコール等の潤滑剤、防腐剤、増粘剤、帯電防止剤、マット剤等の公知の各種添加剤を含有させることもできる。

【0077】本発明にけるインクジェット記録用紙は、インク吸収層を支持体の同一側に2層以上有していてもよい。インク吸収層を複数層設ける場合、少なくとも1層が本発明のインク吸収層であればよく、他の層は、ゼラチン等の親水性バインダーを主体とした膨潤層であっても、本発明のインク吸収層であってもよい。

【0078】本発明のインクジェット記録用紙において、インク吸収性を設けた側の反対側に、カール防止、印字直後に重ね合わせた際のくっ付きの防止、他のインクジェット記録用紙にインクが転写するのを防止するために、種々の種類のバック層を設けることが好ましい。

【0079】バック層には、支持体の種類や厚み、インク吸収層の構成や厚みによって変化し一定ではないが、一般には親水性バインダーや疎水性バインダーが用いられる。通常、バック層の厚みは  $0.1 \sim 10\text{ }\mu\text{m}$  の範囲で選ばれる。

【0080】また、バック層は、他の記録用紙とのくっ付き防止、筆記性の改良、さらにはインクジェット記録装置内での搬送性の改良のために表面を粗面化することができる。粗面化には、粒径が  $2 \sim 20\text{ }\mu\text{m}$  の有機または無機の微粒子を用いることができる。

【0081】インクジェット記録用紙において、非吸水性支持体としては、従来、インクジェット用記録用紙に用いられていた公知の非吸水性支持体を適宜使用できる。これら非吸水性支持体としては、例えば、ポリエステル系樹脂、ジアセテート系樹脂、トリアセテート系樹脂、アクリル系樹脂、ポリカーボネート系樹脂、ポリ塩化ビニル系樹脂、ポリイミド系樹脂、セロハン、セルロイド等の材料からなる透明フィルム、あるいは、基紙の少なくとも一方に白色顔料等を添加したポリオレフィン樹脂からなる被覆層を設けた樹脂被覆紙(いわゆるRCペーパー)、ポリエチレンテレフタレートに白色顔料を添加した、いわゆるホワイトペット等の半透明もしくは不透明支持体が用いられる。

【0082】支持体とインク吸収層との接着強度を大きくする等の目的で、インク吸収層の塗布に先立って、コロナ放電処理や下引処理等を行うことが好ましい。さら

に、本発明のインクジェット記録用紙は、必ずしも、無色透明とか白色である必要はなく、着色された記録シートであってもよい。

【0083】両面をポリエチレンでラミネートした紙支持体を用いたインクジェット記録用紙は、記録画像が写真画質に近くしかも低コストで高品質の画像が得られるために特に好ましい。

【0084】以下、ポリエチレンでラミネートした紙支持体について説明する。

【0085】紙支持体の原紙は、木材パルプを主原料とし、必要に応じて、ポリプロピレンなどの合成パルプあるいはナイロンやポリエステルなどの合成繊維を加えて抄紙される。木材パルプとしては、LBKP、LBSP、NBKP、NBSP、LDP、NDP、LUKP、NUKPのいずれも用いることができるが、短繊維分の多いLBKP、NBSP、LBSP、NDP、LDPをより多く用いることが好ましい。但し、LBSP及びまたはLDPの比率は10重量%以上、70重量%以下が好ましい。

【0086】パルプは、不純物の少ない化学パルプ（例えば、硫酸塩パルプ、亜硫酸塩パルプ）が好ましく、また、漂白処理を行って白色度を向上させたパルプも有用である。

【0087】原紙中には、高級脂肪酸、アルキルケテンダイマー等のサイズ剤、炭酸カルシウム、タルク、酸化チタンなどの白色顔料、スターチ、ポリアクリルアミド、ポリビニルアルコール等の紙力増強剤、蛍光増白剤、ポリエチレングリコール類等の水分保持剤、分散剤、4級アンモニウム等の柔軟化剤などを適宜添加することができる。

【0088】抄紙に使用するパルプの濾水度は、CSFの規定で200～500ccが好ましく、また、叩解後の繊維長がJIS-P-8207に規定される24メッシュ残分の重量%と42メッシュ残分の重量%との和が30乃至70%が好ましい。なお、4メッシュ残分の重量%は20重量%以下であることが好ましい。

【0089】原紙の坪量は30乃至250gが好ましく、特に、50乃至200gが好ましい。原紙の厚さは40乃至250 $\mu$ mが好ましい。

【0090】原紙は抄紙段階または抄紙後にカレンダー処理して高平滑性を与えることもできる。原紙密度は0.7乃至1.2g/m<sup>2</sup>（JIS-P-8118）が一般的である。更に原紙剛度はJIS-P-8143に規定される条件で20乃至200gが好ましい。

【0091】原紙表面には表面サイズ剤を塗布してもよく、表面サイズ剤としては前記原紙中添加できるサイズ剤と同様のサイズ剤を使用できる。

【0092】原紙のpHは、JIS-P-8113で規定された熱水抽出法により測定された場合、5～9であることが好ましい。

【0093】原紙表面及び裏面を被覆するポリエチレンは、主として低密度のポリエチレン（LDPE）及び／または高密度のポリエチレン（HDPE）であるが、他の線状低密度ポリエチレン（LLDPE）やポリプロピレン等も使用することができる。

【0094】インク吸収層側のポリエチレン層は、写真用印画紙で広く行われているように、ポリエチレン中にルチルまたはアナターゼ型の酸化チタンを添加して不透明度及び白色度を改良したものが好ましい。酸化チタンの含有量はポリエチレンに対して概ね3～20重量%、好ましくは4～13重量%である。

【0095】ポリエチレン被覆紙は、光沢紙として用いることも、また、ポリエチレンを原紙表面上に溶融押し出してコーティングする際にいわゆる型付け処理を行って通常の写真印画紙で得られるようなマット面や絹目面を形成して用いることもできる。

【0096】原紙の表裏のポリエチレンの使用量は、インク吸収層やバック層を設けた後で低湿及び高湿化で保存されたときにカールがないように選択される。通常、インク吸収層側のポリエチレン層の厚さを20～40 $\mu$ m、バック層側のポリエチレン層の厚さを10～30 $\mu$ mの範囲とする。

【0097】本発明において、以下の特性を有しているポリエチレン被覆紙支持体を好ましく用いることができる。

【0098】①引っ張り強さ：JIS-P-8113で規定される強度で縦方向が2乃至30Kg、横方向が1乃至20Kg

②引き裂き強度：JIS-P-8116による規定方法で縦方向が10乃至200g、横方向が20乃至200g

③圧縮弾性率：103Kgf/cm<sup>2</sup>以上

④表面ベック平滑度：光沢紙として用いる場合はJIS-P-8119に規定される条件で20秒以上（いわゆる型付け品に合ってはこれ以下であってもよい。）

⑤不透明度＝直線光入射／拡散光透過条件の測定条件で、可視域の光線での透過率が20%以下、特に、15%以下

本発明のインクジェット記録用紙の構成層、即ち、空隙型のインク吸収層や必要に応じて適宜設けられる下引き層などの種々の構成層は、公知の方法を用いて形成することができる。好ましい形成方法は、各層を構成する塗布液を支持体上に塗布し乾燥する方法である。2層以上を同時に塗布することもでき、この場合、全ての親水性バインダー層の塗布を1回の塗布で済ます、同時塗布方法が好ましい。

【0099】塗布方法としては、ロールコーティング法、ロッドバーコーティング法、エアナイフコーティング法、スプレーコーティング法、カーテン塗布方法あるいは米国特許第2681294号明細書記載のホッパーを使用するエクストルージョンコート法が好ましく用いられる。

【0100】次に、本発明のインクジェット記録用紙を用いてインクジェット記録するとき使用する水性記録液について説明する。

【0101】水性記録液は、通常、水溶性染料、溶媒及び必要に応じて添加されるその他の添加剤からなっている。水溶性染料としては、公知の、インクジェット記録で用いられている直接染料、酸性染料、塩基性染料、反応性染料あるいは食品用色素等の水溶性染料が使用できるが、直接染料または酸性染料が好ましい。

【0102】水性記録液の溶媒は、水を主体とするが、水性記録液が乾燥した際に染料が析出し、ノズル先端や水性記録液の供給経路で目詰まりを起こすのを防止するために、沸点が120℃以上で室温で液状の高沸点有機溶媒が添加される。高沸点有機溶媒は、水が蒸発した際に染料などの固形成分が析出し、粗大析出物の発生を防止する作用を有することが必要であり、そのために、水よりはるかに低い蒸気圧を有することが要求される。また、水に対する混和性が高い必要がある。

【0103】そのような目的で用いられる高沸点有機溶媒としては、例えば、エチレングリコール、プロピレングリコール、ジエチレングリコール、トリエチレングリコール、グリセリン、ジエチレングリコールモノメチルエーテル、ジエチレングリコールモノブチルエーテル、トリエチレングリコールモノブチルエーテル、グリセリンモノメチルエーテル、1, 2, 3-ブタントリオール、1, 2, 4-ブタントリオール、1, 2, 4-ペンタントリオール、1, 2, 6-ヘキサントリオール、チオジグリコール、トリエタノールアミン、ポリエチレングリコール（平均分子量が約300以下）等のアルコール類が挙げられる。また、上記した以外にも、ジメチルホルムアミド、N-メチルピロリドン等も使用できる。

【0104】これら多くの高沸点有機溶剤の中でも、ジエチレングリコール、トリエタノールアミンやグリセリン、トリエタノールアミン等の多価アルコール類、トリエチレングリコールモノブチルエーテル等の多価アルコールの低級アルキルエーテル等は好ましいものである。

【0105】水性記録液に必要なに応じて添加されるその他の添加剤としては、例えば、pH調節剤、金属封鎖剤、防カビ剤、粘度調整剤、表面張力調整剤、湿潤剤、界面活性剤、防錆剤等が挙げられる。

【0106】水性記録液は、記録用紙に対する濡れ性を良好にしたり、インクジェットノズルからの吐出を安定化させる目的で、25℃において、25~50dyne/cm、好ましくは28~40dyne/cmの範囲内の表面張力を有するのが好ましい。

【0107】また、水性記録液の粘度は、通常25℃にお

いて2~10Cpが好ましく、更に好ましくは2.5~8Cpである。また、水性記録液のpHは3~9が好ましい。インクノズルから吐出されるインク液滴の容量が1~30pLである場合、記録紙上で約20~60μmの直径のドット径が得られるので好ましい。このようなドット径で印字されたカラープリントは高画質の画像を与える。更に好ましい最小インク液滴の容量は2~20pLである。

【0108】また、少なくともマゼンタ及びシアンについて、濃度が2倍以上異なる2種類の水性記録液を用いた記録方式でインクジェット記録する場合、ハイライト部では低濃度のインクが使用されるためにドットの識別がしにくくなるが、本発明は、かかる記録方式を用いた場合にも用いることができる。

【0109】インクジェット記録方法において、記録方法としては、従来公知の各種の方式を用いることができる。記録方法の詳細は、例えば、インクジェット記録技術の動向（中村孝一編、平成7年3月31日、日本科学情報株式会社発行）に記載されている。

【0110】

【実施例】以下に、本発明を実施例により具体的に説明するが、本発明はこれらの実施例によって限定されるものではない。

【0111】実施例1

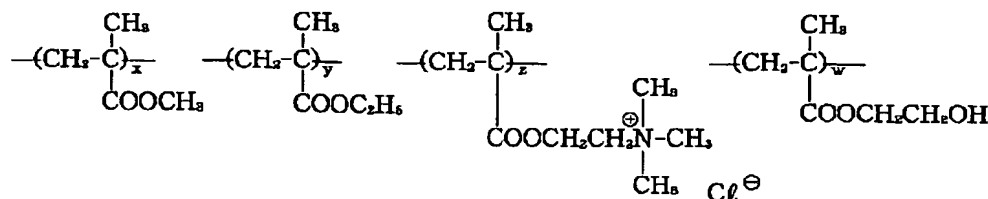
160g/m<sup>2</sup>の写真用原紙の両面をポリエチレンで被覆した紙支持体（記録面側には厚さ35μmのアナターゼ型二酸化チタンを13重量%含有するポリエチレン層が形成されており、裏面側には厚みは25μmでポリエチレン層が形成され、その上にT<sub>g</sub>=65℃のアクリル系ラテックス樹脂を固形成分として0.6g/m<sup>2</sup>及び平均粒径が約13μmのシリカをマット剤として0.3g/m<sup>2</sup>含有するバック層が形成されている。）を用意した。

【0112】次に、純水900ml中に、1次粒子の平均粒径が約7nmの微粒子シリカ粉末180gを高速ホモジナイザーで攪拌しながら添加しシリカ水分散液を作製した。次に、このシリカ水分散液中に、下記のカチオン性媒染剤の20%水溶液を120ml添加し、30分間高速ホモジナイザーで分散して青白い澄明な分散液を得た。次に、平均重合度が3500でケン化度が88%の5%ポリビニルアルコール水溶液（酢酸エチルを4重量%含有）400mlを徐々に添加した。次いで、硬膜剤として5%ほう酸水溶液（20%エタノール含有）を表1に示す量を添加し、更に、10%ゼラチン水溶液を50ml加えた後、全量を純水で2100mlに仕上げて空隙層を形成する塗布液を作製した。

【0113】

【化1】

## カチオン性媒染剤



$$x : y : z : w = 25 : 25 : 45 : 5 \text{ (モル比)}$$

$$\text{平均分子量} \approx 23,000$$

10

【0114】次いで、上記のようにして得られた塗布液を40℃に加温し、上記ポリエチレンで被覆した紙支持体の記録面側に湿潤膜厚が220 $\mu\text{m}$ になるように塗布し、塗布皮膜温度が15℃以下になるように冷却させた（20秒間）。次いで、25℃の風を60秒間、30℃の風を60秒間、40℃の風を60秒間、45℃の風を120秒間、更に35℃の風を60秒間順次吹き付けて乾燥し、更に、25℃、相対湿度50%の雰囲気を通気させて調湿して記録用紙1～5を作製した。

## 【イエローインク-1】

ダイレクトイエロー86	2.0 g
ジエチレングリコール	22.2 g
グリセリン	4.5 g

純水で100mlに仕上げる。

## 【マゼンタインク-1】

ダイレクトレッド227	1.8 g
グリセリン	3.5 g
ジエチレングリコールモノブチルエーテル	21.5 g

純水で100mlに仕上げる。

## 【シアンインク-1】

ダイレクトブルー199	2.4 g
エチレングリコール	16.1 g
グリセリン	9.5 g

純水で100mlに仕上げる。

【0118】上記の各インクジェット用水性記録液100ml当たりの水酸基数は以下の通りである。

【イエローインク-1】：566ミリモル/100ml

【マゼンタインク-1】：247ミリモル/100ml

【シアンインク-1】：829ミリモル/100ml

次に、インクジェット用水性記録液を使用してオンデマンド型インクジェットプリンター（液滴容量=25pL、最大印字密度=720dpi×720dpi）で記録用紙1～20に印字した。印字はそれぞれ単色ベタ、2色ベタ、3色ベタ印字で行った。

【0115】上記記録用紙1～5において、平均重合度が3500でケン化度が88%の5%ポリビニルアルコール水溶液の量を500mlにした記録用紙6～10、600mlにした記録用紙11～15及び800mlにした記録用紙16～20を同様にして作製した。

【0116】得られた記録用紙1～20を35℃で3日間保存した。

【0117】次に、インクジェット用水性記録液を以下の通り調製した。

20

【0119】印字する際には、単色ベタ印字はそれぞれ最大印字密度（インク量=20ml/m<sup>2</sup>）で行い、2色印字は各色とも最大印字密度の60%（インク量=24ml/m<sup>2</sup>）、3色ベタは最大印字密度の40%（インク量=24ml/m<sup>2</sup>）で行った。

【0120】このときの各ベタ部での高沸点有機溶媒に由来する水酸基の量は表2に示す通りである（ミリモル/m<sup>2</sup>）。

【0121】

【表2】



単色ベタ			2色ベタ			3色ベタ
Y	M	C	Y+M	M+C	C+Y	Y+M+C
113	49	166	98	129	167	131

【0122】表2から、この水性記録液の上記印字条件におけるZ（水性記録液を記録用紙に最大吐出量で印字したとき、印字された記録用紙の単位面積あたりに含まれる高沸点有機溶媒中の水酸基量のうちの最大の水酸基量）は167ミリモル/m<sup>2</sup>である。

【0123】印字した記録用紙1～20を40℃、相対湿度80%で2日間保存した。保存した試料の膜面のひび割れ状況をルーペを用い目視で確認し、以下の評価基準で評価した。

（評価基準）

- ◎：ルーペで確認してもひび割れが発生していない  
○：ルーペでは確認できるが目視だけでは判別できないひび割れが発生している  
△：目視で僅かにひび割れが発生しているのがわかる  
×：目視で激しいひび割れが発生しているのがわかる。

【0124】得られた結果を表3に示した。

【0125】

【表3】

記録用紙No.	ほう酸		PVAの水酸基数(Y)	$\frac{X}{Y}$	$\frac{Z}{Y}$	保存後ひび割れ						
	ml	X				Y	M	C	Y+M	M+C	C+Y	Y+M+C
1 比較例	30	2.5	37.6	0.066	4.44	△	○	×	○	△	×	△
2 比較例	60	5.1	37.6	0.136	4.44	○	◎	×	◎	○	×	○
3 比較例	90	7.6	37.6	0.202	4.44	○	◎	×	◎	○	×	○
4 比較例	150	12.7	37.6	0.338	4.44	○	○	×	○	○	×	○
5 比較例	300	25.3	37.6	0.872	4.44	△	○	×	×	△	×	△
6 本発明	30	2.5	47.0	0.053	3.55	△	○	△	◎	○	△	○
7 本発明	60	5.1	47.0	0.109	3.55	◎	◎	○	◎	◎	○	◎
8 本発明	90	7.6	47.0	0.162	3.55	◎	◎	○	◎	◎	○	◎
9 本発明	150	12.7	47.0	0.270	3.55	◎	◎	○	◎	◎	○	◎
10 比較例	300	25.3	47.0	0.538	3.55	○	◎	×	△	○	×	○
11 比較例	30	2.5	56.4	0.044	2.98	△	○	×	△	○	×	○
12 本発明	60	5.1	56.4	0.091	2.98	○	◎	○	○	○	○	○
13 本発明	90	7.6	56.4	0.136	2.98	◎	◎	◎	◎	◎	◎	◎
14 本発明	150	12.7	56.4	0.226	2.98	◎	◎	◎	◎	◎	◎	◎
15 本発明	300	25.3	56.4	0.452	2.98	◎	◎	○	◎	◎	○	◎
16 比較例	30	2.5	75.2	0.033	2.23	△	○	×	○	○	×	○
17 本発明	60	5.1	75.2	0.068	2.23	◎	◎	○	◎	◎	○	◎
18 本発明	90	7.6	75.2	0.101	2.23	◎	◎	◎	◎	◎	◎	◎
19 本発明	150	12.7	75.2	0.169	2.23	◎	◎	◎	◎	◎	◎	◎
20 本発明	300	25.3	75.2	0.337	2.23	◎	◎	◎	◎	◎	◎	◎

【0126】表3の結果から、本発明の条件①と条件②を共に満足する場合、高温・高湿下で保存してもベタ印字部にひび割れが生じないことがわかる。

【0127】特に、 $X/Y$ が0.1以上0.4以下、 $Z/Y$ が3以下のときにもっともひび割れが少ないことがわかる。

【0128】実施例2

インクジェット用水性記録液を以下の通り調製した。

〔イエローインク－2〕

ダイレクトイエロー86 2.0 g  
ジエチレングリコール 21.5 g  
グリセリン 9.8 g

純水で100mlに仕上げる。

〔マゼンタインク－2〕

ダイレクトレッド227 1.8 g  
グリセリン 10.5 g  
ジエチレングリコール 19.5 g

純水で100mlに仕上げる。

〔シアンインク－2〕

ダイレクトブルー199 2.4 g  
エチレングリコール 16.1 g  
グリセリン 12.9 g

純水で100mlに仕上げる。

【0129】上記の各インクジェット用水性記録液100ml当たりの水酸基数は以下の通りである。

〔イエローインク－1〕：725ミリモル/100ml

〔マゼンタインク－1〕：710ミリモル/100ml

〔シアンインク－1〕：940ミリモル/100ml

実施例1で使用したオンデマンド型インクジェットプリンターを用いて、実施例1に記載の印字条件で、単色ベタ、2色ベタ、3色ベタ印字した。

【0130】このときの各ベタ部での高沸点有機溶媒に

由来する水酸基の量は表4に示す通りである（ミリモル／ $\text{m}^2$ ）。

【0131】

【表4】

単色ベタ			2色ベタ			3色ベタ
Y	M	C	Y+M	M+C	C+Y	Y+M+C
145	142	188	172	198	200	190

【0132】表4から、この水性記録液の上記印字条件におけるZ（水性記録液を記録用紙に最大吐出量で印字したとき、印字された記録用紙の単位面積あたりに含まれる高沸点有機溶媒中の水酸基量のうちの最大の水酸基量）は200ミリモル／ $\text{m}^2$ である。

【0133】次いで、印字して得られた記録用紙1～2

0について、実施例1と同様にして膜面のひび割れ状況を評価した。

【0134】得られた結果を表5に示す。

【0135】

【表5】

記録用紙No.	ほう酸		PVAの水酸基数(Y)	$\frac{X}{Y}$	$\frac{Z}{Y}$	保存後ひび割れ						
	ml	X				Y	M	C	Y+M	M+C	C+Y	Y+M+C
1 比較例	30	2.5	37.6	0.066	5.32	×	×	×	×	×	×	×
2 比較例	60	5.1	37.6	0.136	5.32	△	△	×	×	×	×	×
3 比較例	90	7.6	37.6	0.202	5.32	△	△	×	×	×	×	×
4 比較例	150	12.7	37.6	0.338	5.32	○	○	×	×	×	×	×
5 比較例	300	25.3	37.6	0.672	5.32	△	△	×	×	×	×	×
6 比較例	30	2.5	47.0	0.053	4.25	×	×	×	×	×	×	×
7 比較例	60	5.1	47.0	0.109	4.25	○	○	×	×	×	×	×
8 比較例	90	7.6	47.0	0.162	4.25	○	○	△	△	×	×	×
9 比較例	150	12.7	47.0	0.270	4.25	○	○	△	△	×	×	×
10 比較例	300	25.3	47.0	0.538	4.25	△	△	×	×	×	×	×
11 比較例	30	2.5	56.4	0.044	3.55	×	×	×	×	×	×	×
12 本発明	60	5.1	56.4	0.091	3.55	○	○	○	○	○	○	○
13 本発明	90	7.6	56.4	0.136	3.55	◎	◎	○	○	○	○	○
14 本発明	150	12.7	56.4	0.226	3.55	◎	◎	○	○	○	○	○
15 本発明	300	25.3	56.4	0.452	3.55	○	○	○	○	○	○	○
16 比較例	30	2.5	75.2	0.033	2.67	×	×	×	×	×	×	×
17 本発明	60	5.1	75.2	0.068	2.67	◎	◎	○	○	○	○	○
18 本発明	90	7.6	75.2	0.101	2.67	◎	◎	◎	◎	◎	◎	◎
19 本発明	150	12.7	75.2	0.169	2.67	◎	◎	◎	◎	◎	◎	◎
20 本発明	300	25.3	75.2	0.337	2.67	◎	◎	◎	◎	◎	◎	◎

【0136】表5の結果から、実施例1と同様に、本発明の条件①と条件②を共に満足する場合、いずれも高温・高温下で保存してもひび割れがほとんど生じていないか全く生じていないことがわかる。

【0137】

【発明の効果】本発明のインクジェット記録方法によれば、高温高湿下で保存しても、ひび割れを生じない印字記録を得ることができる。

フロントページの続き

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